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FUNDAMENTALS
OF
PHYSICAL CHEMISTRY

For Students of Chemistry and Related Sciences

BY

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TRANSLATED AND ADAPTED
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FIRST EDITION
THIRD IMPRESSION

McGRAW-HILL BOOK COMPANY, INC.
NEW YORK: 370 SEVENTH AVENUE
LONDON. 6 & 8 BOUVERIE ST., E. C. 4
1925

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McGraw-Hill Book Company, Inc.

PRINTED IN THE UNITED STATES OF AMERICA

THE MAPLE PRESS COMPANY, YORK, PA.

TRANSLATORS' PREFACE

In view of the number of excellent books on physical chemistry now available in the English language, it may be wondered why anyone should venture to present a translation of a foreign text at the present time. The translators believe, however, that there is still room for a text in which kinetic theory, thermodynamics, and quantum theory, each being discussed upon the basis of experimental facts, are considered of equal importance for the development of the subject. Professor Eucken's "Grundriss der physikalischen Chemie" is written from this viewpoint. The discussion of the recent important developments in the study of the structure of matter, the excellence of the kinetic treatment of physicochemical problems, and the correlation of kinetic theory and thermodynamics are also prominent features of this book

Owing to the scarcity of American and English publications in Germany during the past few years, it was considered desirable to supplement the original work with material which the author was unable to obtain, together with some which has appeared since the second German edition was prepared. The larger portion of this material has been incorporated in the form of over 150 footnotes and a few short insertions in the text which do not affect the author's treatment.

In those portions dealing with solutions, there have been so many new developments which we felt should be incorporated, especially in view of the important position which this subject occupies in American chemistry, that we also considered it desirable to extend the discussion of the thermodynamics of solutions given by Professor Eucken. It was soon found that this necessitated entirely rewriting the empirical and thermodynamic subdivisions under solutions in Sec. B; the author's kinetic treatment has remained unchanged.

In making this adaptation, the subject has been approached from the standpoint of the ideal or perfect concentrated solution, which we believe follows quite logically upon the author's treatment of ideal gases and ideal solids. The introduction of the concept of the perfect solution made it necessary as well as advantageous to introduce the activity concept in Sec. C (**188*b*, 188*c*, 191, 195, 211**). A comparison of the first and second German editions indicated that Professor Eucken himself was considering such a treatment.

In writing these portions every effort was made to adhere closely to the form and style of the remainder of the book. The translators would be the first to admit that the result in these two respects is not perfect. In correspondence, Professor Eucken has stated that he intends to alter and extend considerably his own treatment of solutions in the next edition. At the present time, however, the most satisfactory procedure seemed to be to incorporate the new material in the way which we have adopted, rather than to relegate such important subject matter to an appendix, although this latter alternative would have involved far less labor on our part. This field is changing so rapidly, as is well known, that it is quite possible that Professor Eucken's future treatment of solutions may differ considerably from ours. We are indebted to Professor Eucken for reviewing the major portion of the footnotes and new material which have been incorporated and for offering suggestions and criticisms regarding them.

All of the adaptations, as well as the footnotes, for which the translators are solely responsible, are indicated by asterisks. The translators have also made a number of important changes in the original nomenclature, nearly all of which were due to the individual peculiarities of the two languages Due to the scope of the subject matter and the multiplicity of symbols which this involves, the author was not able to conform completely with the official nomenclature of the International Commission as published in the *Z. Elektrochem.*, **27**, 527 (1921); for the same reason the translators were not able to conform as completely with present American usage as they desired.

The translators have freely consulted a number of textbooks on physical chemistry and monographs on special subjects for information. Since these works are quoted in the text and footnotes, no special mention will be made at this point, except to acknowledge the assistance which Washburn's "Principles of Physical Chemistry," Lewis and Randall's "Thermodynamics," and Hildebrand's "Solubility" have given in the development of the subject of solutions. We wish to thank Dr. H. C. Urey for reading the manuscript of Sec. D and for the valuable suggestions he has given on a number of points; also Dr. W. F. Meggers for the photograph of the band spectrum of nitrogen.

E. R. J.
V. K. L.

DEPARTMENT OF CHEMISTRY,
COLUMBIA UNIVERSITY,
NEW YORK, N Y
March, 1925.

PREFACE TO THE SECOND EDITION

The basis of the present edition, as has already been emphasized in the preface to the first edition, is a predominantly physical treatment of physicochemical phenomena; in this the use of simple mathematical tools cannot be avoided. Incidentally, this viewpoint, which determines the basis and the structure of the book, has found the approval of a number of colleagues; only a relatively small number found occasion to express fundamental criticisms In view of the theoretical difficulties which are involved in the successful teaching of physical chemistry, the existence of a number of different treatments can be understood and is justified, especially since there is no definite agreement as to the ultimate aim of the teaching. I agree with those colleagues who decline to use a more mathematical-physical treatment of physical chemistry, but only when their object consists in giving a general (as a rule, rather superficial) understanding of physicochemical phenomena. But when it is desired to make accessible to students the resources of physical chemistry which are so useful for practical purposes, the task is made more difficult instead of easier for both teacher and pupil in the attempt to avoid mathematics. That the use of mathematical formulas in the teaching of physical chemistry, with the appropriate adjustment on the part of the teacher, can be performed successfully is shown by the results in analogous subjects—for example, in engineering—for there is no doubt that the students of this subject can actually attain the mathematical preparation essential to it. Should not this be possible for the majority of students of chemistry also?

Although I have adhered essentially to the use of mathematics in the new edition, I have, however, endeavored to simplify several of the more involved developments which give the beginning student difficulties; for example, in the derivation of the fundamental Helmholtz equation $A + U = T\left(\frac{\delta A}{\delta T}\right)$. On account of significant advances made in the more recent work of N. Bohr, several paragraphs in the section on "The Structure of Matter" required reorganization. Suggestions as to a number of minor additions and improvements were very kindly given me by Messrs Buchwald, Herzfeld, Krüger, Paneth, and Volmer, to whom I wish to express my thanks.

A. EUCKEN.

BRESLAU, 1924.

PREFACE TO THE FIRST EDITION

During the last twenty years of the preceding century a new science, "physical chemistry," was created in which physical methods were employed for the investigation of chemical problems. This new science was founded upon fundamental researches by van't Hoff, Arrhenius, and Nernst, and at that period it was both justifiable and desirable to consider it as a separate science. During the past ten years, however, it has become more and more difficult to maintain the individuality of physical chemistry as a science in view of the manner in which both physics and chemistry have developed. Today many physicists are engaged upon a fundamental problem of chemistry in their investigation of the structures of atoms and molecules. On the other hand, many chemists are using purely physical methods in their work. It has thus become unnecessary to have a separate science between physics and chemistry, since there is really no principle which would serve to distinguish it from either.

If, however, this viewpoint is set aside and the problems involved in teaching physics and chemistry so that the student shall be able to combine them in his work are considered, the situation appears in a different light.

The chemist and the physicist have modes of thinking and methods of attacking problems which are so different in their natures that it is difficult for the majority of students to unite them and apply them profitably. Experience has shown that, unless both physics and chemistry are taught with particular care, the difficulties involved can be overcome only to a small degree. From the teacher's viewpoint, the justice of considering physical chemistry as a special subject can scarcely be disputed, if one aspires to a fusion of the methods of physics and chemistry for the solution of fundamental problems.

It is hoped that this presentation will be of service in this direction. It is intended especially for students of chemistry, in order to introduce them to the most important points of view and the results of investigations in those branches of modern physics which are closely related to chemistry. The newer textbooks of general and inorganic chemistry usually consider numerous physicochemical laws and principles from a chemical viewpoint. I have assumed that this book, which is written from the physical viewpoint and is therefore a complement to the chemistry textbooks, will be found desirable.

Experience has shown that the mathematical formulas customarily employed in physics present great difficulties to the deeper penetration of physical chemistry for many students of chemistry. It might, therefore, seem tempting to try to eliminate mathematics as much as possible from physical chemistry. By so doing, however, we should deprive ourselves of one of the most valuable aids which our science has at its disposal. Only he who is not frightened away by a simple mathematical formula can expect to derive any real and practical benefit from physical chemistry. In this presentation the use of mathematics will not be avoided when it is of material assistance.

The amount of pure mathematics required for the teaching of physical chemistry is rather small. Beyond a few rules for calculating, it is chiefly necessary to have a certain understanding of the physical meaning of a formula. However, it is this aspect of mathematics, *i.e.*, the interpretation of formulas, which gives the student great difficulties. In order to eliminate these difficulties as far as possible at the very beginning, the main portion on physical chemistry is preceded by a short mathematical-physical introduction in which the most important fundamental concepts involved are touched upon. This introduction does not, of course, claim to offer a complete substitute for attending a course of lectures on mathematics nor for the reading of a detailed book suitable for self study.

In order to make the scope of the work as concise as a textbook demands, numerous limitations became imperative. It was endeavored to develop the fundamentals of the subject as highly as possible, and therefore but little space has been devoted to the enumeration of isolated facts and empirical rules of lesser significance.

In those cases in which various theories exist concerning one range of phenomena between which no final judgment can be made at present, I was generally compelled to restrict myself to the presentation of only one of them. I endeavored to make the selection in such a way that a somewhat homogeneous style would be preserved throughout the work. Naturally, such a selection is affected by the personal viewpoint of the author. The omission of any particular theory must, therefore, not be considered as an absolutely final rejection based upon fundamental scientific principles

In the choice of references to the literature, I was led by the desire merely to indicate the way to the original literature of the subject concerned. The references are generally limited to single papers which serve to introduce the reader to the literature of the subject, or, where possible, to papers containing a summary of the literature of the particular field An even approximately complete guidance to the literature was not considered to be within the scope of this book. Since an investigator often consults one of the larger, comprehensive works on the special subject in question before searching through the literature himself, it may be mentioned that a clearly arranged, systematic catalogue of books which appeared up to 1914 and which cover the entire field of physical chemistry is to be found in the first volume of the "Lehrbuch der physikalischen Chemie," by K. Jellinek.

Experimental methods were described only in so far as they appeared necessary for their theoretical understanding and for the mathematical application of the formulas. It was not considered essential to include in this book descriptions of methods for performing practical investigations, especially in view of the fact that there are already many books (large and small) which can be recommended for this purpose. As an example, "Physikalische-chemische Übungen," by W. A. Roth (3rd ed , I am especially grateful to Dr. Hermann Senftleben, who in the reading of the manuscript and proof has assisted me by many hints and suggestions of improvement. I am also indebted to Dipl.-Eng. Ernst Karwat for drawing a number of figures and checking some of the calculations.

The publishing firms of Gebr. Borntrager in Berlin, Ferdinand Enke in Stuttgart, Wilhelm Knapp in Halle, Julius Springer in Berlin, and Fr. Vieweg and Son in Braunschweig, were very kind in transferring to us the stereotype plates of a number of illustrations which had originally appeared in works published by them, and in this place I wish to express my gratitude to these firms.

A. EUCKEN.

BRESLAU, 1922

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SYMBOLS

The page numbers accompanying the various symbols indicate where they occur for the first time or where they are defined. Paragraph references are in bold face type

A	Atomic weight (weight of a gram-atom) Work (usually mechanical) (p. 41)
$A_{T,p}$ $A_{T,v}$	Maximum work under particular conditions of restraint (footnote, p 54).
$\bar{A}_{T,p}$	Chemical potential (pp 54, 319)
A_0	Ionic activity of a metal (p 383).
Å	Angstrom, 1Å. = 10^{-8} *cm*
a	Any constant quantity, special first van der Waals' constant (p 129) The activity (p 319) Radius or major axis of an electron orbit (p. 529).
α	Thermal (cubic) coefficient of expansion $\frac{1}{v_0}\left(\frac{dv}{dT}\right)_p$. Bronsted-Debye coefficient (p. 329). Degree of dissociation (p 289).
α', α''	Apparent degrees of dissociation of strong electrolytes (p 315).
b	Any constant term; special, second van der Waals' constant (p 129) Proportionality factor for an elastic force (p 27) Average effective diameter of ions in Debye-Huckel theory (p 332).
β	Empirical constant Degree of association (p 359)
C C_p C_v	Molecular or atomic heat in general or under special conditions of restraint (p 39 et seq)
c	Concentration (moles/*L*). Velocity of light (3 10^{10}*cm* /*sec*)
c'	Concentration (moles/1000 g solvent).
[c]	Mean specific heat (p. 38).
D	Diffusion constant (p 30) Dielectric constant (p. 326).
Δ	Difference Distance between atoms or molecules (pp 473, 648).

δ	Density.
∂	Partial differential.
E	Potential difference (electrical) (p. 42)
E_0	Electrode potential referred to the normal hydrogen electrode (p. 386)
e	Base of the natural logarithms (p. 21)
	Electrical charge
e_0	Elementary charge of electricity (sometimes represented merely by e).
e_k	Charge on nucleus.
ϵ	Energy quantum (p. 113)
	Sometimes electrical charge (**188c**).
F	Number of degrees of freedom (p. 254).
$\mathfrak{F}$	"The Faraday" = 96500 *coulombs*
f	A general function.
	Activity coefficient of solute (p. 320)
	Frictional resistance (p. 26)
ζ	Coefficient of internal friction (p. 243)
η	Coefficient of internal friction (p. 150)
g	Acceleration due to gravity
γ	Ratio of specific heats $\frac{C_p}{C_v}$ (p. 83)
h	Height (p. 147)
	Planck's elementary quantum of action (6.55 10^{-27} *erg sec.*) (p. 559)
H	Strength of magnetic field (p. 504)
H	$= U + pv =$ Gibbs' heat function (p. 54).
H'	$= -H =$ heat content of reaction at constant pressure (p. 364).
I, i	Electrical current strength (p. 43)
i	(True) chemical constant (p. 188)
	Van't Hoff's osmotic coefficient (p. 307)
i'	Conventional chemical constant (p. 418)
J	Moment of inertia (pp. 465, 595).
	Heat of ionization (p. 624)
	Integration constant in Nernst Heat Theorem (p. 105).
K	Equilibrium constant of the mass-action law (p. 286).
K_a	The same referred to activities
K_c	The same referred to concentrations (p. 290).
K_p	The same referred to partial pressure (p. 290)
K_{sp}	Solubility product (p. 356).
$\mathfrak{K}$	Force.

k	Boltzmann's constant = gas constant for a single molecule = $\frac{R}{\mathbf{N}}$. Reaction velocity constant (p. 428) Radioactive disintegration constant (p. 18)
κ	Compressibility $\frac{1}{v}\left(\frac{dv}{dp}\right)_T$ (p. 57) Debye's reciprocal distance (p. 327). Specific conductivity (p. 303)
L	Mean kinetic energy (p. 88)
$L.M.A.$	Law of Mass Action
l	Mean free path (p. 92)
ln	Natural logarithm (p. 20)
log	(= $\log_{10}$) Decadic or Briggsian logarithms.
Λ or Λ_v	Heat of vaporization
Λ_f	Heat of fusion
Λ_s	Heat of sublimation
Λ_c	Molecular or equivalent conductivity at finite concentration (p. 304)
Λ_∞	The same at infinite dilution (p. 304)
λ	Wave length
M	Molecular weight (weight of one "mole")
M_a	Average molecular weight (p. 290)
m	Mass Current number (quantum theory) (p. 555) Any whole number.
μ	Unit of length 0.0001 cm, $\mu\mu = 10^{-7}$ cm Number of revolutions per second (p. 556). The ionic strength (p. 328)
N	Number of actual molecules Mole fraction of a solution (p. 201).
$\mathbf{N}$	Avogadro's number (p. 65)
n	Any whole number Number of components Number of moles True quantum number
n_e	Valence or number of charges on an ion.
n_r	Refractive index (p. 641).
n^*	Effective quantum number (p. 572).
ν	True frequency (number of vibrations per second) (pp. 28, 554). Number of ions in a molecule (p. 323)
ν'	Wave number (number of light waves per centimeter in a vacuum) (p. 544).

O, o	Surface (pp. 42, 151)
ω	Angular velocity.
P	Potential energy Number of phases (p. 254). Total pressure
p	Gas pressure. External pressure
p°	Vapor pressure of a pure component (p 207).
Π	Osmotic pressure (p. 203)
Π_i	Internal pressure (p 154)
π	Number = 3.1416 Reduced pressure (p. 168) Cohesion pressure (p 138)
π_0	Critical pressure (p. 164).
Q	Quantity of heat (p 37).
q	Cross-section, surface
R	General gas constant (p 76) for numerical values see Table 1.
$\mathfrak{R}$	Rydberg's constant (p 554)
ρ	Average density of electricity (p 324).
S	Entropy (p 58).
s	Solubility (p 322) Distance
Σ	Summation.
σ	Surface tension (p 146).
T	Absolute temperature (p. 37)
T_c	Centigrade temperature (p 37)
T_M	Melting or freezing point of a solution (p 216).
t	Time
Θ	Characteristic temperature (p 101)
ϑ	Reduced temperature (p 168)
ϑ_0	Critical temperature (p 164).
τ	Half-life period (p 24).
U	Internal energy (p. 45). Velocity of ionic migration (p 302).
U_o	Null-point energy (p 122).
U'	Heat of reaction at constant volume (p. 363).
ι^-	Ionic mobilities (p 443).
V, v	Volumes
v_M	Molecular volume (pp. 76, 292).
V	Velocity.

$\mathbf{V}_l$	Velocity of light.
φ	A general function. Angular measure Reduced pressure (p 168). Osmotic coefficient (p 321)
φ_0	Critical volume (p. 164).
ψ	Average electrical potential in Debye-Huckel theory (p. 324).
w	Probability (p 69) Specific resistance (p 303)
w_k	Heat capacity (p 38).
x, y	Variable quantities
X	Strength of electrical field $= \dfrac{dE}{ds}$ (p 42)
Z	number, *e g*, nuclear change number, atomic number, etc.
Z^*	Effective nuclear charge (p 572)
z	Valence of an ion (**188c**).
$\simeq$	Approximately equal to
$\sim$	Is proportional to

FUNDAMENTALS OF PHYSICAL CHEMISTRY

SECTION A

MATHEMATICAL-PHYSICAL INTRODUCTION

1. The Physical Law as a Mathematical Function.—If the real task of physical chemistry is considered to be the application of physical methods to the solution of chemical problems, then it becomes appropriate to emphasize some of the characteristic features of physical investigation at the very beginning of this study.

The aim of modern physical research is to discover and to investigate the relations which exist between the various simple characteristics of substances, such as mass, velocity, pressure, volume, temperature, etc. Such an interdependence of physical quantities, in so far as it can be formulated exactly, is called a physical law.

The language of ordinary life does not lend itself to expressing the peculiarities of physical laws. At best, words can be used only to supplement the other means of expression. The physicist considers it of secondary importance to discuss a law in non-mathematical terms, and to do so exclusively, as has been attempted in some books, is uneconomical and unsatisfactory.

It is absolutely necessary for every student who wishes to master the physical laws, whether for practical or for theoretical purposes, to familiarize himself with the other more profitable methods of expression. Efforts in this direction are always well repaid.

The physical magnitudes involved in the law are expressed by numbers. This is one of the characteristic features of physical laws, the importance of which is not sufficiently emphasized by the ordinary means of expression. A reciprocal dependence of several variable magnitudes (the **variables**) is indicated in mathematical terminology as a **function.**

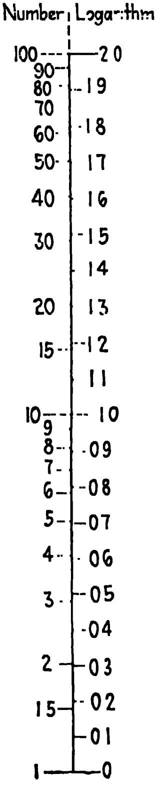

FIG. 1

2. Different Methods of Representing a Function.—From its definition as an arrangement of two or more series of numbers, it is at once evident that a function may be expressed in the form of a table, such as the table of logarithms or the table showing the variation of the density of air with temperature and pressure. In the latter example there are three variables. There is a disadvantage in the tabular representation, however, in that only a limited number of points can be arranged with respect to each other, although this form of presentation does have the advantage of accuracy. The remaining points must be found by a mathematical interpolation.

This inconvenience is avoided if the function be plotted as a curve in a plane or as a surface in space; at the same time a better idea is obtained of the behavior of the function. But when compared with the tabular method, the conveniences of this graphic representation are often secured at the expense of accuracy.

A function with only two variables is usually represented as a curve on a plane, the latter being defined by two coordinates at right angles with the point of intersection reckoned as zero. The horizontal coordinate is called the **abscissa;** the vertical one, the **ordinate.** The graphic method is so common that a description of the method of application is unnecessary. It can be applied to any law or function in which two or more numerical values are related to each other. If there are three variables, the *complete* function can only be represented by a surface in space. Sometimes, however, it is convenient to keep the one variable constant and plot the other two at different values of the first. A family of curves (see Fig. 28) is then obtained.

Up to a certain point, the advantages of tabular and graphic representation may be united by means of nomographical methods.[1] For each of the variables a special scale is made. If there are only two variables, the two scales are simply placed beside each other; each point on the line of contact between the two scales corresponds to the pair of values of the variables which belong together. An example of a simple nomogram is given in Fig. 1, representing the logarithmic function.

With three variables (Fig. 2), the individual points are arranged on scales of appropriate dimensions and placed in certain definite

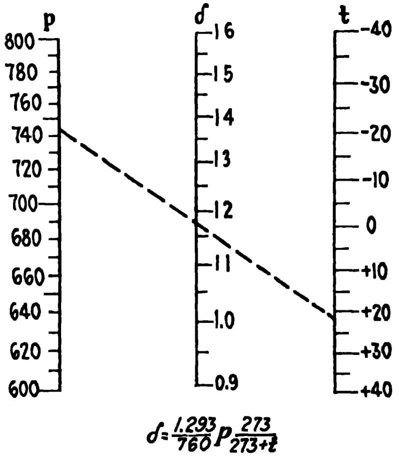

FIG. 2.

positions with respect to each other. A straight line is passed through the proper points on two of the scales and the point of intersection with the scale of the third variable gives the desired value of the latter. In order to read the nomogram in Fig. 2, which represents the dependence of the weight δ of a liter of gas upon the barometric pressure p and temperature t, only a ruler (preferably transparent) is required. For example, at a pressure of 746 *mm.* and a temperature of 22°C., the weight of a liter of air is found (dotted line) to be 1.174 *g*. As W. Biltz and Hüttig[2] have shown, the nomographical methods are excellent for the interpretation of certain thermochemical functions.

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[1] * DEMING, H. G., "Manual of Chemical Nomography," University of Illinois Press (1918).

[2] *Z. anorg. Chem.*, **109**, 111 (1919).

3. The Function as a Mathematical Formula.—It is the custom to express a function of two variables by the symbol

$$y = f(x). \qquad (1)$$

The quantities x, y, the **variables,** are frequently differentiated as "independent" and as "dependent" variables, in Eq. (1), x is the independent and y the dependent variable. If it is desired to reverse this in order to obtain y as the independent and x as the dependent variable, then Eq. (1) must be transformed into

$$x = \varphi(y). \qquad (1a)$$

The two functions $f(x)$ and $\varphi(y)$, representing the same dependence, are called **inverse functions.** A simple example of a function and its corresponding inverse function is

$$y = x^2 \text{ and } x = \sqrt{y}.$$

Nature does not distinguish between x and y as independent and dependent variables; the distinction is made for purely practical purposes When this distinction is of no importance, the **implicit** representation

$$F(x, y) = 0$$

is to be recommended in place of the **explicit** forms (Eqs. (1) and (1a)).

The expression of a function by means of a formula is important because it can then be represented by any of the other methods. Besides, from it all the characteristics of the function may be read directly, although sometimes a mathematical transformation is expedient. Some of the mathematical operations, such as differentiation, integration, and the like, are briefly reviewed in the remainder of this section. As far as possible, the examples will be so chosen that they may be directly applied in the later chapters.

4. Linear Functions.—A particularly simple function is expressed by the equation

$$y = b'x + a. \qquad (2)$$

A physical example of this is the variation of the volume of a gas with temperature T_c (Centigrade):

$$v = v_0(1 + \alpha T_c) = v_0 + v_0\alpha T_c,$$

in which v_0 is the volume at 0°C and α the **coefficient of expansion.**

The conversion of the Centigrade temperature x into the Fahrenheit temperature y offers a further example:

$$y = 9/5\, x + 32.$$

The most primitive means of establishing the course of such a function consists in calculating y from a series of values of x and expressing them as a table. The points x, y so established are then plotted on rectangular coordinates and joined by the simplest possible curve. In this way it is found that Eq. (2) represents a straight line. At the same time its special characteristics, *e.g.*, its point of intersection with the axes, its slope, etc., may be read off directly. The geometrical characteristics of the important function shown in Eq. (2) may be exactly ascertained in the following manner:

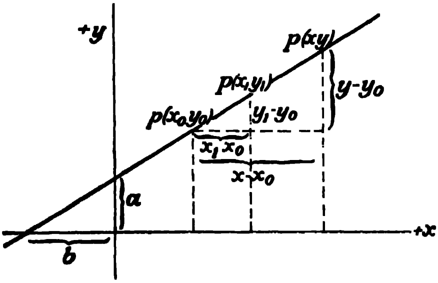

Fig. 3

If $f(x)$ represents a straight line, then for the variable point xy, when compared with two fixed points x_0y_0 and x_1y_1, the proportion (Fig. 3)

$$\frac{x - x_0}{x_1 - x_0} = \frac{y - y_0}{y_1 - y_0}$$

must always be satisfied. But this may be brought into the form

$$y = \frac{y_1 - y_0}{x_1 - x_0}x + \frac{x_1y_0 - x_0y_1}{x_1 - x_0},$$

which becomes identical with Eq. (2) if

$$b' = \frac{y_1 - y_0}{x_1 - x_0};\ a = \frac{x_1y_0 - x_0y_1}{x_1 - x_0}.$$

At the same time the geometrical significance of b' and a appears: $b' = \frac{y_1 - y_0}{x_1 - x_0}$ represents the tangent of the angle between the straight line and the x-axis, the magnitude of which is a measure of the slope of the straight line. Moreover, the ratio b' is frequently used in place of the angle as a measure of the slope.

The points of intersection of the straight line with the axes are found most simply if Eq. (2) is stated in the form

$$\frac{x}{b} + \frac{y}{a} = 1,$$

where b is substituted for $\frac{-a}{b'}$. If $x = 0$, then $y = a$, and when $y = 0$, $x = b$. Therefore, the straight line cuts the y-axis at a distance a from the zero point and the x-axis at a distance b (compare Fig. 3).

5. The "Slope" of a Curve. The Differential Coefficient.—From geometrical as well as from physical considerations, the straight line is of especial importance, because all curves which show no sudden breaks or discontinuities in their course can be replaced over very short distances by straight lines. The entire function may thus be represented by an exceedingly large number of very short straight lines or *line elements* joined together in a series and gradually changing slope throughout. In order to obtain an exact duplication of a curve in this way, it is essential to have an infinite number of such line elements, but in practical cases only a relatively small number is necessary to obtain a sufficiently accurate result. If, for example, a circle is replaced by an inscribed n-sided polygon, then the difference between the circumference of the circle and the polygon is 1.66 per cent when $n = 10$, 0.28 per cent when $n = 25$, and only 0.06 per cent when $n = 50$.

The slope of the curve is found by taking the slope of the line element at the desired point, but the curve itself is distinguished from the line element in that its slope changes continuously.

From the geometrical as well as the physical standpoint, a knowledge of the slope of a curve (function) is of particular interest. It is, therefore, important to be able to calculate the slope by means of a general and universally applicable process, **differentiation.**

Consider the two points x_1y_1 and x_0y_0 (Fig. 4) lying on a curve and that a finite distance $\Delta x = x_1 - x_0$ and $\Delta y = y_1 - y_0$ separates them. Then the expression

$$b' = \frac{y_1 - y_0}{x_1 - x_0} = \frac{\Delta y}{\Delta x}$$

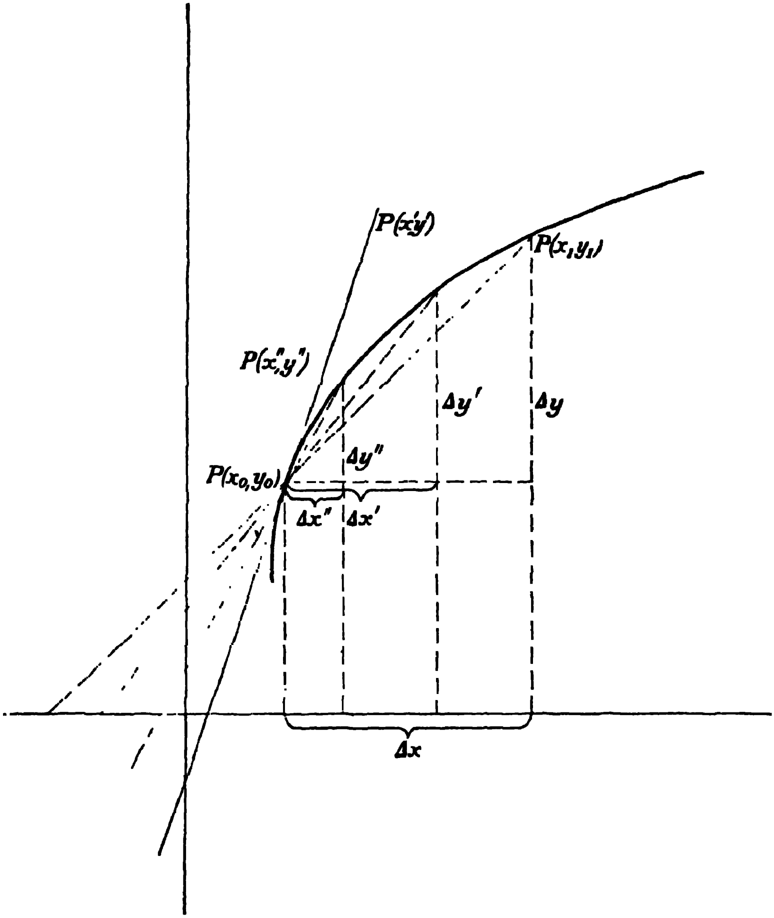

FIG 4

may be designated as the slope of the curve just as in Eq. (2). This expression, which is usually called the **difference coefficient,** involves only the *mean* slope of the curve between the two points. In order to find the slope at the point x_0y_0 itself, the point x_1y_1

must be pushed closer and closer to x_0y_0. The distances Δy and Δx thus become smaller and smaller ($\Delta x'$, $\Delta y'$ as well as $\Delta x''$, $\Delta y''$ in Fig. 4) until it approaches the value zero. The slope at any point xy on a curve is represented by the *limiting value of the ratio* $\frac{\Delta y}{\Delta x}$ for a vanishing value of Δx. This is usually written:

$$\lim_{\Delta x = 0} \frac{\Delta y}{\Delta x} = \frac{dy}{dx} = f'(x) \tag{3}$$

and $\frac{dy}{dx}$ is called the **differential coefficient** of the function $y = f(x)$. Since in irregular curves (*i.e.*, not circles) this generally changes from point to point, it is likewise a function of x, generally designated by $f'(x)$, which is known as the **derivative** of the function $f(x)$.

Although the above, exact definition of the differential quotient demands that the quantities dx and dy, the so-called **differentials**, should be infinitely small, yet, as a rule, no very large error is introduced when finite values are retained for the differences Δx and Δy, even when the resulting quotient is put equal to the differential quotient. For example, the difference quotient of the function $y = x^2$ in the neighborhood of $x = 1$ assumes the following values according to the values of Δx or Δy

$$\frac{\Delta y}{\Delta x} = \frac{1.0201 - 1.0000}{1.010 - 1.000} = \frac{0.0201}{0.010} = 2.01,$$

$$\frac{\Delta y}{\Delta x} = \frac{1.002001 - 1.000000}{1.001 - 1.000} = \frac{0.002001}{0.001} = 2.001,$$

while the differential quotient, for which the general formula $y' = 2x$ holds according to Eq. (4), has the value 2.000 when $x = 1$.

The magnitudes of the differences which can be put equal to the differential quotient to a sufficient degree of approximation varies a great deal from case to case. In numerous cases in which the differential quotient has a physical or chemical significance (*cf.* 8), it is possible to use differences, which are more conveniently measured directly, in place of differentials without introducing any important error

6. Calculation of the Differential Coefficient.—In order to calculate the differential coefficient for definite functions, it is convenient to start from the difference coefficient; *i.e.*, the expression

$$\frac{\Delta y}{\Delta x} = \frac{f(x + \Delta x) - f(x)}{\Delta x} \tag{3a}$$

is first developed and then Δx is gradually made vanishingly small. In the function

$$y = f(x) = x^n$$

the binomial theorem gives

$$f(x + \Delta x) = x^n + nx^{n-1}\,\Delta x + \frac{n(n-1)}{1\cdot 2}x^{n-2}\,\Delta x^2 + \quad .$$

If this expression is substituted in Eq. (3*a*), the term x^n is eliminated. If Δx now assumes continuously decreasing values, then the terms with Δx^2, Δx^3, etc. vanish and there remains

$$\lim_{\Delta x = 0} \frac{\Delta y}{\Delta x} = \frac{dy}{dx} = nx^{n-1}. \tag{4}$$

In a similar manner, all continuous functions represented by formulas may be differentiated. As examples may be given

$$y = \sin x; \qquad \frac{dy}{dx} = \cos x \tag{5}$$

$$y = \cos x; \qquad \frac{dy}{dx} = -\sin x \tag{6}$$

which were obtained through the use of Eq. (3*a*) with the relation

$$\sin(\alpha + \beta) = \sin\alpha \cdot \cos\beta + \cos\alpha\,\sin\beta$$

and proceeding to the limiting case where Δx becomes vanishingly small. The following expressions, in which u and v represent various functions of x, are very often used:

$$y = u \pm v; \qquad \frac{dy}{dx} = \frac{du}{dx} \pm \frac{dv}{dx} \tag{7}$$

$$y = u \cdot v; \qquad \frac{dy}{dx} = u\frac{dv}{dx} + v\frac{du}{dx} \tag{8}$$

$$y = \frac{u}{v}; \qquad \frac{dy}{dx} = \frac{v\frac{du}{dx} - u\frac{dv}{dx}}{v^2}. \tag{9}$$

A special case of Eq. (8) which occurs very frequently is where u is a constant A. In this case

$$y = Av; \qquad \frac{dy}{dx} = A\frac{dv}{dx}, \tag{8a}$$

since the differential coefficient of a constant quantity is always equal to zero. For the differentiation of more complex functions of x, but which, by means of suitable substitutions, such as $u = \psi(x)$; $w = \varphi(u)$; $y = f(w)$, can be brought into the form $y = f[\varphi(u)]$, the following relation is frequently used:

$$\frac{dy}{dx} = \frac{dy}{dw}\,\frac{dw}{du}\,\frac{du}{dx}. \tag{10}$$

Just as by the differentiation of a function $f(x)$ its derivative $f'(x)$ is obtained, so by differentiating $f'(x)$ the second differential coefficient or the second derivative of $f(x)$ is found.

$$\frac{df'(x)}{dx} = \frac{d^2f(x)}{dx^2} = f''(x). \tag{11}$$

7. Maxima, Minima, and Points of Inflection.—The geometrical significance of the first differential coefficient has been discussed sufficiently above. It is frequently of interest to search for those places at which the slope of the curve is zero, and therefore, where the condition $f'(x) = 0$ is fulfilled. At such a point, the tangent to the curve must be parallel to the abscissa; the curve must possess either a *maximum* or a *minimum* if the third possibility, the appearance of a point of inflection, is disregarded for the present. It is possible to decide which of the two cases exists by means of the second derivative whose sign indicates whether the slope is increasing or decreasing. A positive sign of the second derivative states that the first derivative, *i.e.*, the slope, is increasing, just as a positive sign in the first derivative states that the original function is increasing. Correspondingly, a negative sign for the second derivative shows that the slope of the function is to be considered as decreasing. Therefore, if $f'(x) = 0$ and simultaneously, $f''(x) < 0$, then a maximum exists, since $f'(x) = \tan \alpha$ is first positive (α is an acute angle, therefore $\tan \alpha$ is positive) and then passes through zero into negative values (Fig. 5*a*).

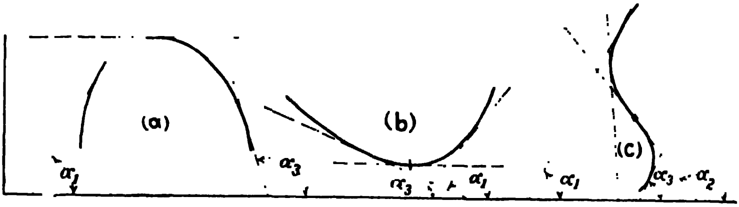

Fig. 5

If $f''(x)$ is positive while $f'(x) = 0$, then $f(x)$ passes through a minimum (Fig. 5*b*), since in this case α changes from an obtuse to an acute angle ($\tan \alpha_1 < \tan \alpha_3$).

If $f''(x)$ vanishes, it indicates that the slope of the curve passes through a maximum or a minimum at the point under consideration—such a point is called a *point of inflection* (Fig. 5c).

The calculation of maximum, minimum, and inflection points on a curve may be simply illustrated by the example:

$$y = x^3 - {}^{15}\!/_{2}x^2 + 18x.$$

The first derivative, calculated by means of Eqs. (4) and (7), is

$$\frac{dy}{dx} = 3x^2 - 15x + 18,$$

which vanishes when $x_1 = +2$ and $x_2 = +3$. To determine whether these points involve a maximum or minimum, the second derivative is taken:

$$f''(x) = \frac{d^2y}{dx^2} = 6x - 15.$$

From this it is found that, at the point $x = 2$, the second derivative is negative and therefore the curve possesses a maximum at this point. A minimum exists at the point $x = 3$, where $f''(x)$ is positive. When $x = {}^5\!/_2$, $f''(x) = 0$ and hence this is the point of inflection. From these data no difficulties are involved in representing the approximate path of the curve.

8. Velocity and Other Physical Differential Coefficients.—In a number of cases the physical significance of the first differential results directly from the idea of the slope of a curve. Functions in which time is the independent variable are often used, *e.g.*, the movement of a point is described by stating its distance s from some definite zero (or starting) point reached after a time t.

$$s = f(t).$$

According to the above, the difference quotient $\frac{\Delta s}{\Delta t}$ signifies the increase Δs of the distance during the time Δt (*e.g.*, one hour) or the distance passed over in unit time. This quantity is known as the **average velocity** $\bar{V}$ for the respective time unit. If t is chosen infinitely small, the differential coefficient is obtained which is the *true* velocity of the body at the time t; namely,

$$\frac{ds}{dt} = V. \tag{12}$$

A relatively large time unit can thus be retained; if, for example, it is said that a railway train has a velocity of 60 *km.* per hour at a definite moment, this does not mean that the train has actually traveled 60 *km.* in an hour, but only says that it would have traveled 60 *km.* if it had continued moving for one hour at the speed measured at that moment.

In a chemical reaction, the amounts of the reacting substances change; as the one increases, the other simultaneously decreases. If any single substance be selected, then during the reaction its concentration (expressed in mols per unit volume) will change in some definite manner with the time, and this change may be expressed by

$$c = f(t).$$

The change of concentration with time $\frac{dc}{dt}$ may obviously be considered as a measure of the velocity of the course of reaction. The expression $\frac{dc}{dt}$ is often simply called the **velocity of reaction.** Similarly, it is customary to designate all other differential quotients with respect to time as a velocity (angular velocity, velocity of precipitation, velocity of solution, etc.). Other similar functions in which the temperature T is the independent variable play an important rôle in physics, *e.g.*, the change of the volume of a body with temperature is expressed by

$$v = f(T).$$

If the temperature increment is made very small, so that it may be assumed to be dT, then the corresponding volume change will be dv. The ratio $\frac{1}{v_0}\frac{\Delta v}{\Delta T}$ is known as the **mean coefficient of expansion over the interval** ΔT; $\frac{1}{v_0}\frac{dv}{dT}$ is the **true coefficient of expansion** *of the body at the temperature* T. A further example of one of the differential quotients used very often in the theory of heat is given by the expression for specific heat (*cf.* **19**).

The second differential coefficient is of major importance in many physical problems. For example, a force is defined as the increase of momentum or impulse which a body undergoes during unit time. Momentum is defined by the product

$$m\mathrm{V} = m\frac{ds}{dt}.$$

The following expression for a force $\mathfrak{K}$ is valid, since m is in general constant

$$\mathfrak{K} = \frac{d(m\mathrm{V})}{dt} = m\frac{d\mathrm{V}}{dt} = m\frac{d\frac{ds}{dt}}{dt} = m\frac{d^2s}{dt^2}. \tag{13}$$

This fundamental equation is identical with the statement of Newton's second law of motion.

9. Integration as the Reverse of Differentiation.—It has been shown how to obtain the differential quotient when a function $y = f(x)$ was assumed. Very often, especially in physical problems, it becomes necessary to solve the reverse problem of finding the original function from the first or second differential. The mathematical operation involved in this process is called **integration.** In many cases this may be performed very simply, as it is only necessary to reverse the process of differentiation. For example, from the expression

$$\frac{dy}{dx} = f'(x) = x^m \tag{14}$$

one immediately obtains the function

$$y = f(x) + Const = \frac{x^{m+1}}{m+1} + Const. \tag{14a}$$

The term *Const.* signifies a constant quantity, because the differentiation of the first term according to Eq. (4) gives x^m and the differential quotient of the constant term is equal to zero. However, in other cases, which will be discussed in detail later on, such a solution is not possible. The reason for this lies in the fact that the reversed process of differentiation often leads to new functions which, in comparison with the derivative $f'(x)$, possess entirely different properties.

Geometrically, a differential equation like Eq. (14) expresses nothing more than that the slope of a curve has a definite magnitude for a definite value of the independent variable x. It gives no means of determining the absolute value of the dependent variable (y). What such a differential equation really states may be translated into a diagram such as Fig. 6. The individual arrows, which describe the differential quotient, are to be connected to form a continuous curve. In this way it is found that, in general, each of the arrows can belong to only one curve, although there are an infinite number of parallel curves each corresponding to a solution of the differential equation. This result has already been formally expressed by the undetermined additive constant in Eq. (14a), because the curves established by Fig. 6 are, indeed, parallel to each other, *i.e.*, the ordinates y of two curves chosen at random differ at corresponding points by a constant amount C'.

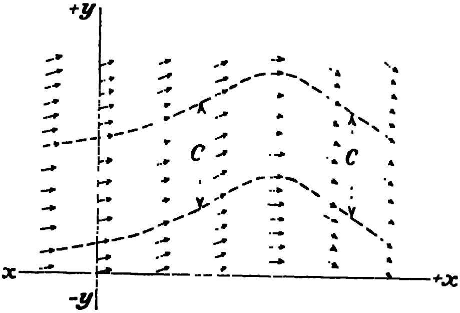

Fig. 6

As a rule, in physical problems only a single, very definite curve is involved; the selection is made so as to fulfil some concrete physical condition, according to which the curve must pass through some definite point, such as x_0y_0 (see **13**).

10. Integration as a Summation.—Suppose that, in analogy to the procedure for $f(x)$, $f'(x)$ is expressed as curves whose ordinates y' are equal to $f'(x)$, which is a different procedure from that in Fig. 6, and let these curves be designated as the **differential curves** (Fig. 7*b*). If, now, it is desired to obtain the integral curve $y = f(x)$, we again start from the difference quotients as follows:

The expression $\frac{\Delta y}{\Delta x} = f'(x)$ is multiplied on both sides by Δx; this is permissible, since Δx always has a finite value. Thus

$$\Delta y = f'(x)\Delta x. \tag{15}$$

The variable y is now obtained directly from a number of individual values of Δy (see Fig. 7*a*), such that

$$y = \Delta y_1 + \Delta y_2 + \Delta y_3 + \quad . \; .$$

or, in abbreviated form,

$$y = \sum_{x=a}^{x=x} \Delta y,$$

where $\sum\limits_{x=a}^{x=x}$ states that the summation is to be carried out between a fixed value $x = a$ and a variable value $x = x$. Introducing Eq. (15),

$$y = \sum_{x=a}^{x=x} f'(x)\Delta x.$$

Proceeding now to the limiting value $\Delta x = 0$, the principle of the considerations will not have changed, but the size of the steps in Fig. 7*a* will become exceedingly small and at the same time the number of steps becomes infinitely large. In other words, the individual steps approach closer and closer to the curve and finally merge into it. For such a sum, which is composed of an exceedingly large number of vanishingly small terms, the integral sign $\int$ has been introduced and

$$y = \lim_{\Delta x = 0} \sum_{x=a}^{x=x} f'(x)\Delta x = \int_a^x f'(x)dx$$

is written. The product $f'(x)\Delta x = y'\Delta x$ is expressed in Fig. 7*b* by the area of a strip with an altitude y' and a width Δx, which is, therefore, the sum of the areas in the entire step-like figure *ABCD*. By proceeding to the limits where Δx is vanishingly small, the area of the step-like figure becomes identical with the area *ABCD* bounded by the curve *DA*, the two ordinates *CD* and *AB*, and the abscissa axis. This, therefore, translates the integral $\int_a^x f'(x)dx$ into geometrical terms. *The integral curve (Fig. 7a) is found from the differential curve (Fig. 7b) because the area between the differential curve, its abscissa axis, one fixed, and one variable ordinate represents a function of* (x).

The figure *ABCD* may be also considered as the difference between the areas *EAB* and *ECD*; the first is a function only of (x), the second the same function of (a), and therefore

$$y = \int_a^x f'(x)dx = f(x) - f(a). \qquad (16a)$$

The integration constant (*Const.*) in Eq. (14*a*) thus acquires a simple geometrical meaning. Since $f(a) = -Const.$ is true, this must represent the area *ECD*. If in Eq. (16*a*) the value of (x) is changed, there is a movement along a definitely determined curve, but if (a) (the *Const.*) is changed, there is a transition to another curve.

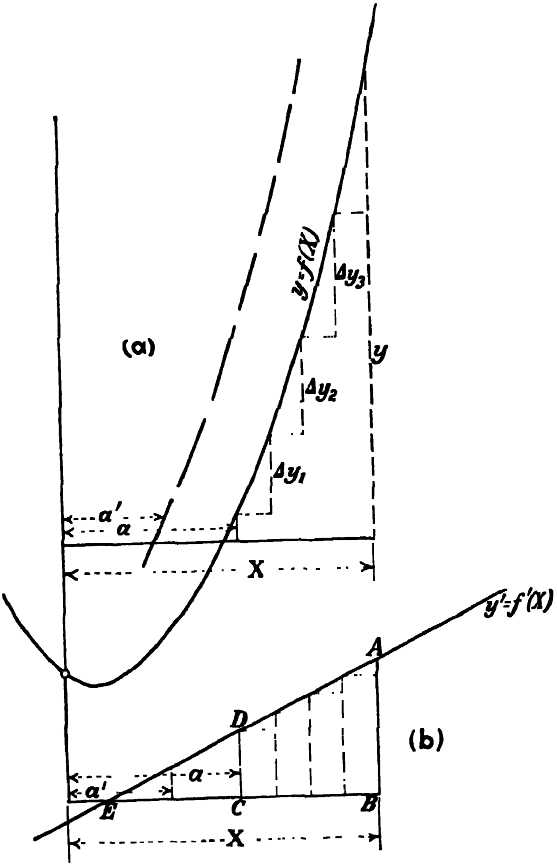

FIG. 7

If the value of (x) as well as (a) is now considered fixed (it is then customary to use (b) instead of (x)), a definite value of (y) is also obtained from

$$y_0 = \int_a^b f'(x)dx = \Big[f(x)\Big]_a^b = f(b) - f(a). \qquad (16b)$$

The form $y_0 = \Big[f(x)\Big]_b^a$ is often convenient because it serves as a transition stage between the undetermined integral $f(x)$ to the definite integral $f(b) - f(a)$.

The fact that the integral in Eq. (16*a*) is equal to the area enclosed between the differential curve $f'(x)$, the abscissa, and the ordinates $f(a)$ and $f'(x)$ makes the integration simple and measuring the area of the figure by some purely practical means is often sufficiently accurate. In general, sufficient accuracy may be had by merely plotting the curve $f'(x)$ on coordinate paper and counting the number of square millimeters or centimeters enclosed It is somewhat more convenient to use the ingeniously constructed planimeter, with which the borders of the figure are followed with the pencil of the apparatus until the starting point is reached and the area of the figure is read directly from the scale.

11. The Significance of the Differential Equation in Physical Problems. The Decomposition of Radioactive Substances. (Introduction).—As previously mentioned, physical problems are much more often concerned with integration than with differentiation. This arises from the following facts: (1) an experiment generally gives only an empirical relation between the final physical variables contained in the form $y = f(x)$, and (2) in the theoretical treatment of a problem it is difficult or even impossible to examine a process of nature completely and represent it by a function of the character $y = f(x)$, so that the test of the theory is not directly feasible. Therefore, the problem must be approached in the following indirect manner: The complete process is split up into a large number of small elementary processes; since each of the latter is considerably simpler than the process taken as a whole, it is often possible to establish a relation between the desired physical variables for each one without much difficulty; by the summation of the effects of all elementary processes, the solution for the entire process is reached. It is clear that the relation which holds for each elementary process is already a differential equation. By the integration (summation) of them is found a relation of the form $y = f(x)$ which is valid for finite numbers of quantities. A direct comparison between the results of the experiments is thus permitted.

A typical case in which a law of the form $y = f(x)$ is obtained by starting with the differential equation is found in observing the decomposition of a radioactive substance. This example at the same time illustrates the above statement that the integration of a relatively simple differential equation often leads to a function with quite different properties.

A radioactive substance is known to decompose in the course of time (see **261** *et seq.*); its weight and the number of its atoms and the physical effects dependent on it (ionizing power, etc.) gradually decrease. It may now be asked if the rate of decrease of the number (x) of the atoms in the substance is some function $x = f(t)$ or, in case this should be true, if the inverse function $t = F(x)$ may be ascertained theoretically on the basis of some simple assumption.

If the number (x) is relatively large and the radioactive preparation be observed only during a short time dt, then one would be compelled to expect from the above that in every similar time interval a quite definite fraction of the atoms existing at the time decomposes. Assume, for example, that the preparation contains 100,000 atoms, and perhaps 100 would decompose during a definite time, but if it contained only 10,000 atoms only 10 could decompose. If the time of observation is doubled, the number of atoms decomposed must have been doubled. If dx represents the number of atoms which decompose in the short time interval dt, then the percentage decrease $-\frac{dx}{x}$ must be constant for a determined value of dt and must be proportional to any change in the value of dt. The expression

$$-\frac{dx}{x} = kdt \qquad (17)$$

is thus obtained, where k represents a constant proportionality factor.

12. Introduction of the Logarithmic Function and Its Characteristics.—One might easily be convinced that, in spite of its simplicity, the integration of this differential equation is not feasible, at least by means of the previous Eq. (14*a*). However, the simplicity of the entire problem, and, finally, an attempt to force a solution by means of some practical procedure, such as **10**, indicates that a solution must exist. The method which leads to an exact result consists in trying to determine the characteristic properties of this unknown integral function $t = F(x)$ from the differential equation. In the present case this actually succeeds. Hence the conviction that $F(x)$ is really not an exception to the earlier statements, but, instead, expresses a quite familiar function.

If for the present k is made to equal to -1, Eq. (17) takes the form

$$\frac{dF(x)}{dx} = \frac{1}{x} \tag{17a}$$

If x' is then substituted for x and $x' = ax$, which, physically speaking, is merely expressing x in a different unit of measurement, then

$$\frac{dF(ax)}{d(ax)} = \frac{1}{ax}$$

According to Eq. (8a), $d(ax) = adx$, and therefore

$$\frac{dF(ax)}{dx} = \frac{1}{x} = \frac{dF(x)}{dx}.$$

From the integration it follows that

$$\int dF(ax) = \int dF(x) + Const.$$

or

$$F(ax) = F(x) + Const.$$

From the family of curves determined by this equation it is possible to select the one for which $x = 1$, $F(x) = 0$, and the following is then obtained:

$$F(a) = Const.$$

$$F(ax) = F(x) + F(a). \tag{18}$$

The function $F(x)$ must, therefore, be peculiar in that the value of the product ax is equal to the sum of the same function with the specific value (a) and (x) as variables.

Now there is a group of functions which fulfils this condition and which are commonly called logarithms. In general, a logarithm is defined by the relation

$$x = b^{\log_b x}, \tag{19}$$

in which b is a constant, the so-called *base of the system of logarithms*. It can be easily shown that this definition leads directly to the addition theorem (Eq. 18), for, putting

$$y = b^{\log_b y}$$

and multiplying by Eq. (19), there follows from an elementary rule (when a quantity raised to a certain power is multiplied by the same quantity raised to the same or another power, the exponents of the quantity are added):

$$xy = b^{\log_b x} \cdot b^{\log_b y} = b^{\log_b x + \log_b y}.$$

According to Eq. (19), however, the exponent must equal the logarithm of the product xy, so that

$$\log_b(xy) = \log_b x + \log_b y. \qquad (18a)$$

It is obvious from the above that there may be as many systems of logarithms as are desired, depending on the value assigned to b. But in the differential Eq. (17a), only one of the possible systems can be used, the one called the **natural** or **Naperian system,** for which the symbol is ln (*logarithmus naturalis*). The behavior of this function is represented in Fig. 8, which shows that the differential quotient is, indeed, proportional to $\frac{1}{x}$; when

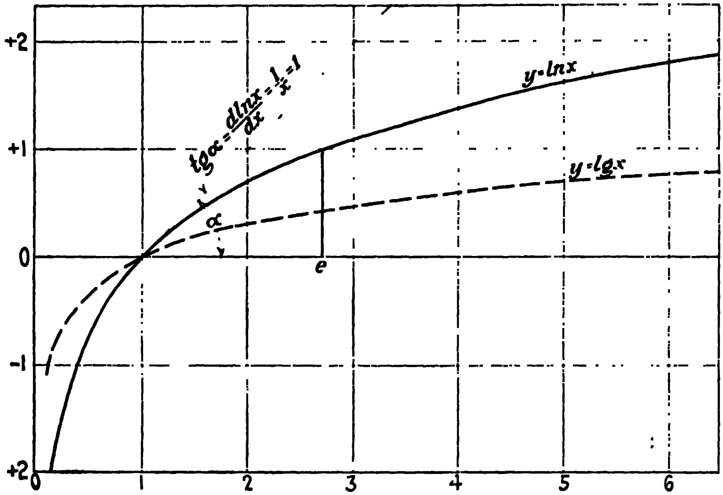

Fig. 8

$$x = 1$$

then

$$\frac{dt}{dx} = 1$$

and

$$\alpha = 45°.$$

The problem of determining the value of the base of the natural logarithms, which is usually represented by e, will now be discussed. According to the above, it is obvious that:

$$t = F(x) = ln\, x \tag{20}$$

or, putting

$$x = 1 + x',$$
$$t = ln(1 + x')$$

and

$$\frac{dt}{dx'} = \frac{1}{1 + x'}, \tag{20a}$$

since

$$dx = dx'.$$

In case x is a real fraction, Eq (20a) may be expressed by the sum s of a geometrical series with the first term $a = 1$ and the quotient $q = -x'$

$$\frac{1}{1 + x'} = 1 - x' + x'^2 - x'^3 + x'^4 - \quad , \tag{21}$$

since, in general, $s = \frac{a}{1 - q}$ Obviously, the smaller the value of x, the shorter the series may be without introducing appreciable error. By integrating Eq. (21) there is obtained directly from (14a)

$$t = ln(1 + x') = x' - \frac{x'^2}{2} + \frac{x'^3}{3} - \frac{x'^4}{4} + \tag{22}$$

Analogously, for

$$\frac{dt'}{dx'} = \frac{1}{1 - x'},$$

$$t' = ln(1 - x') = -x' - \frac{x'^2}{2} - \frac{x'^3}{3} - \frac{x'^4}{4} - \quad . \; . \tag{22a}$$

or, if the last two series are united,

$$ln(1 + x') - ln(1 - x') = ln\frac{1 + x'}{1 - x'} =$$

$$2\left(x' + \frac{x'^3}{3} + \frac{x'^5}{5} + \quad \right). \tag{22b}$$

The "base" of a system of logarithms is obtained from Eq. (19), which is the definition of a logarithm. Putting $x = b = e$, it is obvious that $ln\, e = 1$. Therefore, by investigating Eq. (22*b*) for that value of x' which will make the right-hand side of the equation equal to unity, it is found that approximately $x' = 0.4625 \ldots$ and therefore

$$e = \frac{1 + 0.4625 \ldots}{1 - 0.4625 \ldots} = 2.7183$$

Before concluding the above problem (the rate of decomposition of a radioactive substance), it will be well to discuss another important law depending on the function of the natural logarithm.

If the addition theorem (Eq. (18*a*)) is applied specially to the natural logarithm and making $x = y = e$, the result, after repeating t times, is

$$ln\, e^t = t\, ln\, e \tag{23}$$

or, since $ln\, e = 1$,

$$t = ln\, e^t.$$

A comparison of this formula with Eq. (20) leads directly to the inverse function of the logarithm

$$x = e^t. \tag{24}$$

The differential quotient of this function, the so-called *e*-function or exponential function, results in changing the differential equation for the logarithmic function $\frac{dt}{dx} = \frac{1}{x}$ into $\frac{dx}{dt} = x$. *The exponential function has the characteristic property that its derivative is equal to itself.*

Thus the *e*-function, just as the logarithmic one, may be developed into a series

$$e^t = 1 + t + \frac{t^2}{1 \cdot 2} + \frac{t^3}{1 \cdot 2 \cdot 3} + \cdots \tag{25}$$

That this really reproduces the *e*-function is shown by the fact that its differential quotient is equal to itself (compare Eq. (4)).

The relation between the natural and the common or Briggs' ($b = 10$) systems of logarithms is obtained by merely applying Eq. (19) to first one and then the other system. In this way

$$e^{ln\, x} = x$$
$$10^{\log_{10} x} = x$$

are obtained and therefore $e^{\ln x} = 10^{\log_{10} x}$. Taking logarithms, the result is (compare Eq. (23))

$$\ln x = \ln 10 \log_{10} x = 2.30258 \cdot \log_{10} x = \frac{1}{0.4343} \cdot \log_{10} x. \quad (26)$$

The differential coefficient of the common logarithm, in comparison with that of the natural logarithm, has the value

$$\frac{d \log_{10} x}{dx} = 0.4343 \cdot \frac{d \ln x}{dx} = \frac{0.4343}{x}.$$

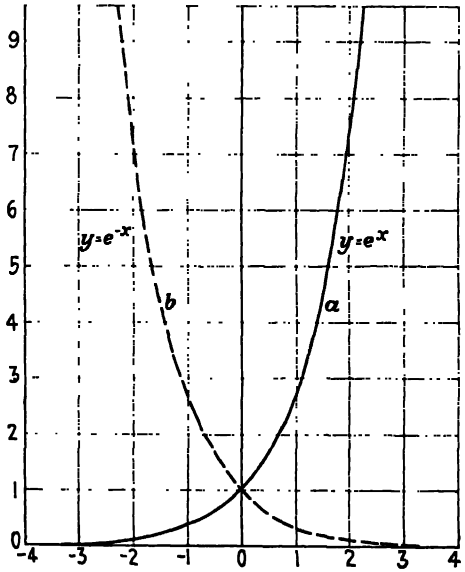

FIG. 9

The behavior of the curves of natural and common logarithms is illustrated in Fig. 8, and that of the exponential function with positive and negative exponents in Fig. 9.

13. The Decomposition of a Radioactive Substance.—The indefinite integral of the original differential Eq. (17) may now be given without further discussion as

$$-\ln x = kt + Const.$$

At the moment the observations begin ($t = 0$), x has the value x_0, and from this

$$Const. = -\ln x_0$$

and therefore

$$kt = ln\, x_0 - ln\, x = ln \frac{x_0}{x} \tag{27}$$

or, if the e-function is introduced,

$$x = x_0\, e^{-kt}. \tag{27a}$$

However, for the radioactive substances it is usually impossible to measure the quantity x directly. On the other hand, during its decomposition the substance sends out a radiation (see **269**), the intensity I of which is directly proportional to the amount of substance decomposed in unit time $-\frac{dx}{dt}$. It is therefore correct to consider that, if the constant terms of the e-function be collected in a single constant C, the result is

$$-\frac{dx}{dt} \sim I = Ce^{-kt}, \tag{27b}$$

an equation which may be directly tested experimentally.

The constant k in the study of radioactivity is known as the **decomposition or radioactive constant**; its reciprocal value $\frac{1}{k}$ is the so-called **average life period**, after which time the number of atoms has diminished to $\frac{1}{e}$ times the value of x, because, when $t = \frac{1}{k}$, the ratio is $\frac{x}{x_0} = \frac{1}{e}$. The **half life period** τ, which is the time required for half the total number of atoms to decompose, is more often used than the decomposition constant k. Its calculation, according to Eq. (27), leads directly to the value

$$k\tau = ln \frac{x_0}{x} = ln\, 2;\ \tau = \frac{1}{k} ln\, 2 = \frac{0.693}{k}.$$

It may be noted that the natural logarithm, or exponential function, is one of the most frequently occurring functions in physics and physical chemistry; it will appear later in widely different kinds of problems. The reason lies in the simplicity of its differential equation. In case a quantity y depends upon an independent variable x, the law may often be found, as the typical example above illustrates, if it is assumed that a definite change dx of x, corresponding to a percentage change in y $\left(i.e., \frac{dy}{y}\right)$, is constant.

14. Integration of Higher Differential Quotients. Motion of a Very Small Particle in a Viscous Medium as Well as under the Influence of an "Elastic Force."—For the integration of a second differential quotient the viewpoints and the rules are the same as those applied to the first differential. It is to be observed, however, that in this case there are generally two undetermined integration constants which must be eliminated on the basis of the fundamental physical limitations selected. In many cases the double integration is not required; the problem can be considered as solved when only the first integration is performed.

As an example of the treatment of the second differential quotient, the behavior of a very small body moving under the influence of a force $\mathfrak{K}$ may be observed. Two cases may be considered.

1. It may be assumed that the force is constant (*e.g*., force of gravity) but that the motion of the body is opposed by a frictional resistance which becomes greater as the velocity increases. The frictional resistance may be conceived as a force $\mathfrak{K}'$, which acts in the opposite direction to the original forward-driving force $\mathfrak{K}$, and for which

$$\mathfrak{K}' = f\mathsf{V}.$$

The total force acting on the body then amounts to $\mathfrak{K} - f\mathsf{V}$, and this quantity is to be used in place of $\mathfrak{K}$ in the equation for Newton's second law (Eq. (13)), so that

$$m\frac{d^2s}{dt^2} = m\frac{d\mathsf{V}}{dt} = \mathfrak{K} - f\mathsf{V}$$

is obtained.

A slight transformation gives

$$\frac{d\mathsf{V}}{\mathfrak{K} - f\mathsf{V}} = \frac{dt}{m},$$

and integration leads to the relation

$$-\frac{1}{f}\,ln(\mathfrak{K} - f\mathsf{V}) = \frac{t}{m} + Const.,$$

the correctness of which, especially with reference to the appearance of the factor $-\frac{1}{f}$, may be proved by differentiation,

taking Eq. (10) into consideration. The fundamental physical limitation says that if $t = 0$, then $v = 0$.
Therefore

$$-\frac{1}{f}\, ln\,\mathfrak{K} = Const.$$

and the final result is

$$v = \frac{\mathfrak{K}}{f}\left(1 - e^{-\frac{ft}{m}}\right), \tag{28}$$

if the e-function is used instead of the logarithm. The term $e^{-\frac{ft}{m}} = e^{-Z}$ is approximately unity for small values of Z; in this

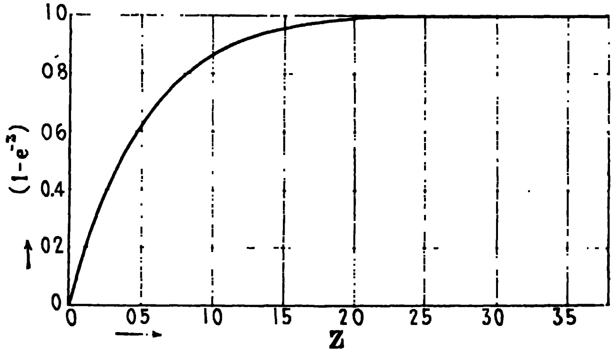

Fig 10

region the velocity of the body is very small. With increasing values of Z, the e-function decreases rapidly and, for large values of Z, becomes practically zero. Accordingly, the velocity of the body rises to a constant limiting value (see Fig. 10), which is given by the expression

$$v_0 = \frac{\mathfrak{K}}{f}. \tag{28a}$$

The smaller the particles (m becomes small) and the greater the frictional force (large value of f) the shorter will be the time in which the limiting value v_0 is attained. Similarly, for the cases to be met in the following chapters, where m approaches molecular dimensions, the time required for the limiting value to be attained is so exceedingly short that the movement of such particles may be calculated directly by means of Eq. (28a).

2. In the second case, let it be assumed that no frictional force exists, but that $\mathfrak{K}$ varies from point to point. A case which is of particular interest is where $\mathfrak{K}$ is an "elastic force," *i.e.*, a force that always seeks to draw the particle back into a definite position of rest. The simplest expression (**Hooke's law**) for an elastic force is

$$\mathfrak{K} = -bx, \tag{29}$$

i.e., the restoring force is directly proportional to the distance of the body from the equilibrium position where $x = 0$ (b is a constant). The combination of Eqs. (13) and (29) yields the equation

$$m\frac{d^2x}{dt^2} = -bx. \tag{29a}$$

A systematic solution of the equation would exceed the bounds of the previous development and it can be disposed of at once, since a general procedure for the integration of such equations does not exist. There is obtained as a solution of Eq. (29*a*)

$$x = x_0 \sin\left(\sqrt{\frac{b}{m}}t + \varphi\right), \tag{30}$$

the correctness of which may be easily demonstrated by two differentiations, taking into consideration Eqs. (5) and (6), and especially Eq. (10). The point performs a sine-wave vibration around the point of equilibrium. In this case both of the abovementioned integration constants are included in x_0, the maximum distance from the point of rest, and φ, the so-called *phase displacement,* but the latter can be neglected without further consideration in the practical application of the equation discussed below, as long as the point of time where $t = 0$ is not fixed physically by the problem. Therefore, φ can be put equal to 0 and also $\frac{\pi}{2}$, in the latter case $x = x_0 \cos \sqrt{\frac{b}{m}}t$ is obtained in place of Eq. (30), since $\sin\left(\alpha + \frac{\pi}{2}\right) = \cos \alpha$.

Now, whenever the term $\sqrt{\frac{b}{m}}t$ increases by a whole number times 2π, Eq. (30) gives quite the same value for x. Therefore, the point has traveled once over its path of vibration, while $\sqrt{\frac{b}{m}}t$ increases by 2π. Therefore, putting $\sqrt{\frac{b}{m}}\tau = 2\pi$, then τ

signifies the period of a single vibration, measured in seconds. If the number of vibrations per second, the **frequency,** is represented by ν_0, then $\nu_0\tau = 1$ or $\nu_0 = \frac{1}{\tau}$.

Then

$$2\pi\nu_0 = \sqrt{\frac{b}{m}}, \tag{31}$$

so that Eq. (30) may also be written as

$$x = x_0 \sin (2\pi\nu_0\tau + \varphi). \tag{30a}$$

15. Functions with More than Two Variables. The Equation of State.—In problems of physical chemistry, functions with two independent variables often appear. An example of this is the **equation of state** of a substance, which is understood to mean a strict relation between the pressure p, the temperature T, and the volume v of a body. As a general example, a given amount of a substance at a definite pressure and definite temperature always occupies a quite definite volume, which may be expressed by

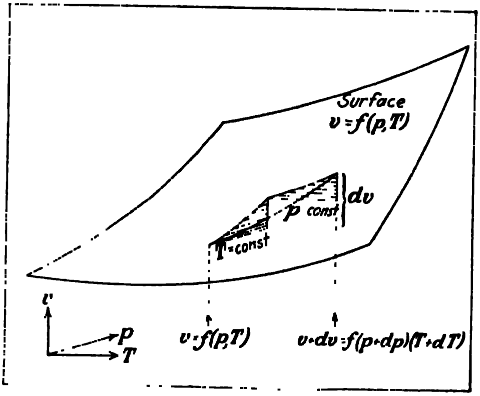

FIG. 11.

$$v = f(p, T) \tag{32}$$

which, in turn, is a simple function, apart from exceptional cases (**112**).

The differentiation of functions with two independent variables may be performed in the same way as a function with only one variable, if one of the variables is temporarily assumed to be constant. Geometrically, this means that the motion is no longer over a surface in space, but on a curve lying on a plane which is perpendicular to the axis of the variable which is being held constant.

A differentiation in which one or more of the variables are held constant is called a **partial differentiation** and is written

$$\frac{dv}{dT} = \left(\frac{\partial v}{\partial T}\right)_p \quad \text{or} \quad dv_1 = \left(\frac{\partial v}{\partial T}\right)_p dT,$$

when p is held constant, and

$$\frac{dv}{dp} = \left(\frac{\partial v}{\partial p}\right)_T \quad \text{or} \quad dv_2 = \left(\frac{\partial v}{\partial p}\right)_T dp,$$

when T is held constant.

If both T and p vary, it can be considered that first one and then the other changes, and the total change is simply the sum or the difference of the two individual changes, depending on whether the two changes act in the same or in opposite directions. Therefore, the above case yields the expression:

$$dv = dv_1 + dv_2 = \left(\frac{\partial v}{\partial T}\right)_p dT + \left(\frac{\partial v}{\partial p}\right)_T dp. \tag{33}$$

Geometrically, this equation means that the transition from a point $v = f(p,T)$ to any neighboring point $v + dv = f(p + dp,\ T + dT)$ need not take place in a single operation. The point may proceed first a distance dp along a plane perpendicular to the T-axis, and later continue its motion for the distance dT on a plane perpendicular to the p-axis (compare Fig. 11).[1]

In case the point moves on the T, p surface in space so that v remains constant and thereby the point moves on a plane perpendicular to the v-axis, dv in Eq. (33) becomes zero, but simultaneously the ratio $\frac{\partial p}{\partial T}$ acquires the same significance as $\left(\frac{\partial p}{\partial T}\right)_v$, and may be written

$$\left(\frac{\partial p}{\partial T}\right)_v = -\frac{\left(\frac{\partial v}{\partial T}\right)_p}{\left(\frac{\partial v}{\partial p}\right)_T}. \tag{34}$$

---

[1] Contrary to Fig. 11, the term $\left(\frac{\partial v}{\partial p}\right)_T$ always has a negative sign in all actual physical processes.

16. Integration of a Partial Differential Equation. The Diffusion of Dissolved Substance as an Example.—While the solution of physical problems with two variables usually starts from one of the ordinary differential equations, the mathematical statement of problems involving more than two variables is usually given as a *partial differential equation.*

To illustrate the peculiarities of a partial differential equation, the theory of diffusion phenomena may be used; this also enters, formally unchanged, into the theory of heat conduction by substituting the temperature T for the concentration c, and the quantity of heat transported for the amount of the diffusing substance. The diffusion occurs in a cylinder of constant cross-section q and only in the direction of the axis of the cylinder.

It may first be assumed that if a concentration c always exists at a point x, at a neighboring point $x + dx$ the concentration $c + dc$ will be maintained. There is, therefore, a concentration difference dc between the two points x and $x + dx$, or at the point x a concentration gradient prevails which is expressed by $+\frac{dc}{dx}$ Diffusion will take place so long as this concentration difference persists. If an amount of substance dn diffuses through the cross-section q along the x-axis in time dt, the law established by Fick states

$$dn = -Dq\frac{dc}{dx}dt, \tag{35}$$

in which D is the **diffusion constant.**

Now imagine another case: In a cylinder open at both ends is a pure solvent, *e.g.*, water. At a certain moment ($t = 0$) a very thin layer (thickness $= 2dx$) of a very concentrated solution is introduced into the cylinder at a point $x = 0$. During the first moment the pure solvent and the concentrated solution bound each other at the points $x = -dx$ and $x = +dx$. As soon as the diffusion begins, the boundaries approach each other more and more closely, and the dissolved particles wander from the middle to both sides. In the middle layer, which was originally very concentrated, the concentration decreases more and more in the course of time. The problem is to find the means of ascertaining the change of concentration of the solvent at individual points, or to find the local change of c at definite points of time, *i.e.*, to discover the function

$$c = f(x, t).$$

Since the course of the process from $x = 0$ is completely symmetrical in both directions, it is obviously sufficient to limit the calculation to the positive values of x.

Consider that in an infinitely long cylinder there is a volume element bounded by two planes perpendicular to the axis of the cylinder and passing through the points x and $x + dx$, so that the dissolved particles wander across. But the concentration in this volume will not be constant; at first it will be zero, then it will increase to a maximum; finally, when all is completely equalized, it will decrease to zero again, since the cylinder is infinitely large. The momentary increase of concentration in the volume element is now $\left(\frac{\partial c}{\partial t}\right)_x$. Its magnitude is simply equal to the excess of the amount of substance entering the layer over the amount leaving it (referred to unit volume).

According to Eq. (35) the amount of substance which in unit time passes the point x into the volume at a determined time t is

$$\frac{dn}{dt} = -Dq\left(\frac{\partial c}{\partial x}\right)_t.$$

The amount of salt which passes out of the volume at the point $x + dx$ is, however,

$$\frac{dn'}{dt} = -Dq\left(\frac{\partial c}{\partial x} + \frac{\partial\frac{\partial c}{\partial x}}{\partial x}dx\right),$$

since the absolute value of $\frac{\partial c}{\partial x}$ at the point $x + dx$ is smaller than at the point x by the amount $\frac{\partial\frac{\partial c}{\partial x}}{\partial x}dx = \frac{\partial^2 c}{\partial x^2}\,dx$. Therefore, the amount of salt increases by

$$\frac{dn - dn'}{dt} = +Dq\left(\frac{\partial^2 c}{\partial x^2}\right)_t dx.$$

Now $q \,.\, dx$ is equal to the volume of the observed elementary cylinder and

$$\frac{dn - dn'}{qdx \cdot dt} = \left(\frac{\partial c}{\partial t}\right)_x,$$

since the concentration is defined as $\frac{n}{v}$. As the general differential equation for the diffusion problem, the result is

$$\left(\frac{\partial c}{\partial t}\right)_x = D\left(\frac{\partial^2 c}{\partial x^2}\right)_t. \tag{36}$$

Since this equation expresses nothing further than that the first partial differential coefficient of one of the variables is equal to the second differential coefficient of the other variable, and this condition is fulfilled by many different functions, it possesses an infinite number of solutions when considered by itself. Due to the existence of a number of physical limiting conditions, a definite solution may be selected from the mass of possibilities. In the above case there are the limiting conditions:

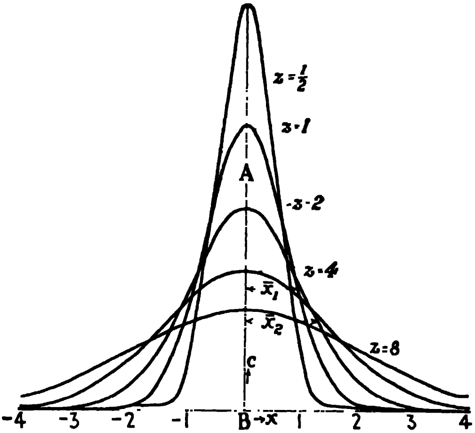

Fig. 12

1. When $t = 0$, $c = 0$ (for all except infinitely small values of x).

2. When $x = 0$, $\frac{\partial c}{\partial x} = 0$ (for all values of t, since through the cross-section at $x = 0$ no diffusion has taken place in any direction).

3. Finally, the total amount of the dissolved substance must be constant, *i.e.*, the sum of the amounts of substance contained in all the elementary volumes at any definite moment must be equal to n, the amount contained in the volume element $q \cdot dx$ at the beginning of the experiment when $x = 0$.

The solution of the differential equation, the systematic derivation of which must likewise be abandoned at this point, gives

$$c = \frac{n_0}{q\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}} \tag{37}$$

or

$$dn = \frac{n_0}{\sqrt{\pi Dt}} e^{-\frac{x^2}{4Dt}} dx, \tag{37a}$$

where dn represents the amount of substance found in a volume element qdx at a point x and at a time t.

One can easily be convinced that Eq. (37) as well as the differential Eq (36) satisfies the initial conditions In investigating condition 3, dn must be integrated over all values from $x = 0$ to $x = \infty$. The integration leads to a new function, the so-called **probability integral**[1] $\Phi(x) = \int_0^y e^{-y^2}dy \left(\text{putting } \frac{x}{\sqrt{4Dt}} = y \text{ and therefore } dy = \frac{x}{\sqrt{4Dt}}\right)$, which assumes the value $\frac{\sqrt{\pi}}{2}$ when $y = \infty$.

A mathematical proof that no other solution of the problem than Eq. (37) exists may be dispensed with, since this must be clear from physical considerations.

Equation (37) is graphically represented in Fig. 12; each curve represents the distribution of concentrations at a definite point of time It is seen that at every point x in the cylinder the concentration c passes through a momentary maximum and that this maximum is smaller and is reached later the larger x becomes. (In Fig. 12, Z should read t.)

17. A Brief Survey of the Following Sections.—In the beginning of 1 it was stated that the chief task of physical chemistry is the application of physical methods to the treatment of chemical problems. The bases for the solution of these problems are exact numerical relations between a number of physical and chemical properties of matter, the discussion of these will therefore form the essential content of the following sections.

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[1] * The probability integral finds extensive application in physics and chemistry, in the theory of errors which give criteria for the rejection of doubtful results in a series of measurements, as well as in the distribution of velocities in the kinetic theory of gases, etc Chapter IX of J. W. MELLOR's "Higher Mathematics for Students of Chemistry and Physics" (Longmans Green & Co. (1919)) should be consulted for a more extensive treatment of these applications of mathematics to chemistry.

Of all the physical magnitudes upon which the behavior of a chemical process depends, temperature is the most important. Therefore in the following presentation the influence of temperature on the chemical behavior of matter will be particularly emphasized. However, it seems appropriate to precede Sec C, in which this problem is attacked directly, by Sec. B, in which a number of general and fundamental laws of thermodynamics and the most important physical and thermal properties of matter are treated. Finally, Sec. D, will be devoted to some of those fundamental properties of matter which are especially important for chemical behavior but at the same time are essentially independent of the temperature

SECTION B

PHYSICAL THERMODYNAMICS

1. GENERAL

a. DEFINITIONS[1]

18. Definition of the Physical Temperature Scale.—Human perception can distinguish qualitatively between warm and cold bodies, but it can make only a rough estimate of that degree of hotness or coldness which is called the temperature. On this account, errors and illusions frequently occur. Therefore, in order to investigate the phenomenon of heat by physical means, there must be first of all a quantitative measure of temperature, *i.e.*, a physically exact temperature scale must be created.

To obtain this measure, two points of temperature are selected which are certain to be different, which on the basis of a general natural law are unchangeable, and which are, moreover, relatively easy to reproduce, the temperature of melting ice and the temperature of water boiling under atmospheric pressure are usually chosen as these two points (Renaldini, 1694) It would, of course, be possible to choose the difference between these two points as the unit of the scale which is to be established, but from practical considerations it is divided into 100 "equal" units. The lower point is called 0 and the upper 100 (Celsius, 1736). Since in the construction of this scale the sensitivity of the human perception of hotness and coldness has not been involved at all, it is evident that some suitable physical device, a "thermometer," must be applied in order to measure the temperature.

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[1] The following presentation is limited to introducing the fundamental concepts of thermodynamics. On the whole, it corresponds to the historic development and suffices for the purpose of physical chemistry. More exact definitions may be found in several textbooks on thermodynamics. The considerations of Carathéodory described by M. BORN (*Physik. Zeit.*, **22**, 218 (1921)) deserve special mention.

As a matter of principle, any physical property which changes with temperature and can be measured with a fair degree of ease and accuracy may be used for the determination of the exact temperature. Properties which are especially suitable for this purpose are the vapor pressure of a substance, the thermoelectric force at the junction of two different metals, the electrical resistance of metals, and the luminosity of radiating bodies. However, the most convenient, although by no means the most accurate, thermometer depends upon the thermal expansion of bodies, especially liquids. The problem stated above, of dividing a given thermometer interval into 100 equal parts, seems at first to offer no difficulties with a thermometer filled with any liquid (*e.g.*, mercury), provided the cross-section of the liquid column is the same throughout its length. The lower temperature is marked 0, the upper 100, and the interval between is divided into 100 parts. But if other liquids are used for filling the thermometer, it is found that, in general, the different thermometers do not indicate the same temperature when compared at some point between 0 and 100.

However, if thermometers filled with gas are used instead of those filled with liquids, the indications agree at all temperatures independent of the kind of gas used. This not only indicates that the various gases expand equally with respect to each other, but also that the absolute value of their expansion coefficients is the same. All gases at constant pressure expand exactly by 0.36604, or $\frac{1}{2.732}$, times their volume between 0 and 100. A complete agreement between gas thermometers will, of course, be obtained only if the pressure of the gas is quite small and the thermometer is not at too low a temperature. Complete agreement can be expected only when the gases are under "ideal conditions" (see **37**).

By means of an ideal gas thermometer the desired definition of the unit (1°) of the temperature scale is found without difficulty. Since the interval (which was defined as 100°) of the volume expansion of an ideal gas corresponds to $\frac{1}{2.732}$ of its volume of 0°, then 1° represents the temperature change during which the volume of an ideal gas (at constant pressure) changes

$\frac{1}{273.2}$ of its volume at 0°. The temperature scale thus established by means of the volume expansion of an ideal gas is identical with the so-called thermodynamic temperature scale which is based upon the second law of thermodynamics, but for the present it is not necessary to consider this point.[1]

As the zero point of the temperature scale either the temperature of melting ice may be retained, thus obtaining for any temperature T_c° the relation:

$$v_{T_c} = v_0 + \frac{1}{273.2} v_0 T_c \quad \text{or} \quad \frac{v_{T_c}}{v_0} = \frac{T_c}{273.2} + 1 = \frac{T_c + 273.2}{273.2}, \tag{38}$$

where v_{T_c} represents the volume of the gas at T_c°; or the temperature may be calculated from $T_c = -273.2$, thus obtaining the **absolute temperature or Kelvin temperature,**

$$T = 273.2 + T_c.$$

Equation (38) then takes the simple form

$$\frac{T}{273.2} = \frac{v_T}{v_0}. \tag{39}$$

In the following the absolute temperature T will be used as much as possible, since this simplifies the majority of the thermodynamic equations.[2]

19. Quantity of Heat, Specific Heat, Molecular Heat.—In order to raise the temperature T_1 of a body A, it is simplest to bring a hotter body B at a temperature T_2 into contact with it. Then the temperatures equalize and both bodies reach the temperature T_x. It may now be imagined that the equalization of heat came about by a certain **quantity of heat** Q flowing from body B to body A. Without entering further into the principles of the question of what is to be understood under the term "heat,"[1] the flow of heat may be considered in much the same way as the flow of a liquid. It can be said that the body B possessed a certain heat content between the temperatures T_x and T_2, just as a vessel contains a certain quantity of liquid between two levels. If the heat content of the body B between the temperature T_x and T_2 is designated by $U'_{x,2}$ and that of the body A between the temperatures T_1 and T_x by $U'_{1,x}$, then from the above it is obvious that

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[1] * More information is to be found in textbooks of thermodynamics· LEWIS, G. N., and RANDALL, M , "Thermodynamics," pp. 51, 135, McGraw-Hill Book Company, Inc (1923), MACDOUGALL, "Thermodynamics and Chemistry," pp. 92 *et seq*, John Wiley & Sons, Inc. (1921); PARTINGTON, "Textbook of Thermodynamics," D Van Nostrand Company (1913), GOODENOUGH, "Principles of Thermodynamics," p. 58, Henry Holt & Company (1920); SCHAEFER, CL., "Einfuhrung in die theoretische Physik," **2**, I, p 164.

[2] From its classification in the absolute system of units, temperature is considered as "dimensionless" Some authors, however, give it a *single dimension T*, others the dimensions of energy.

$$U'_{x,2} = U'_{1,x} = Q. \tag{40}$$

This equation forms the basis of the majority of calorimetric methods of measurement. (If $U'_{1,x}$ is known from an experimental measurement, Q is obtained, and conversely.)

It is clear that the heat content $U'_{1,2}$ of a definite body becomes greater as the temperature difference $T_2 - T_1$ increases. For small increases of temperature in the vicinity of a definite point T_2, the two quantities can be put proportional to each other. The proportionality factor, *i.e.*, the heat content between two temperatures which differ by 1°, is called the **heat capacity** w_k of the body. Thus

$$w_k(T_2 - T_1) = U'_{1,2}. \tag{41}$$

The heat capacity depends upon: (1) the mass m of the substance, (2) on a specific thermal property of the substance, the **specific heat** $[c]$, so that for a uniform body

$$w_k = m[c]$$

or

$$[c] = \frac{U'_{1,2}}{m(T_2 - T_1)} = \frac{u'_{1,2}}{T_2 - T_1}, \tag{41a}$$

where $u'_{1,2} = \dfrac{U'_{1,2}}{m}$ is understood to be the heat content per unit mass. If the body is composed of several uniform substances whose masses are m_1, m_2, m_3 . . . and whose specific heats are $[c_1]$, $[c_2]$, $[c_3]$ . . . , then

$$w_k = m_1[c_1] + m_2[c_2] + m_3[c_3]$$

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[1] An exact answer to this is not possible until after the First Law of Thermodynamics is discussed (**21** *et seq*). In ancient times (up to about the middle of the last century) heat was thought to be of a material nature. (One spoke of "heat matter.")

In many cases it is more convenient to work with the **atomic heat** or **molecular heat** than with the specific heat, these quantities being merely the heat capacity per gram atomic or gram molecular weight:

$$[C] = A[c] \text{ or } = M[c] = \frac{U'_{1,2}}{T_2 - T_1}.$$

As a rule, the specific heat changes with temperature T. Therefore, in order to talk about the specific heat at any particular temperature T, the difference $T_2 - T_1$ must be infinitely small, *i e*, the difference term in Eq. (41*a*) must be replaced by the differential. At the same time the heat content must become infinitely small, so that the result is

$$c = \frac{du}{dT} \quad \text{or} \quad C = \frac{dU}{dT} \tag{42}$$

and in view of Eq. (40)

$$c = \frac{dq}{dT} \quad \text{or} \quad C = \frac{dQ}{dT}. \tag{42a}$$

The specific heat defined by Eq. (42) will be called the **true specific heat** or the atomic or molecular heat at the temperature T. The specific heat $[c]$ defined by Eq. (41*a*) will be called the **mean specific heat** between T_2 and T_1.

Since by integrating Eq. (42) the result is

$$U_{1,2} = \int_{T_1}^{T_2} C dT, \tag{42b}$$

it follows that the relation between the mean and the true specific heats is

$$[C] = \frac{U_{1,2}}{T_2 - T_1} = \frac{\int_{T_1}^{T_2} C dT}{T_2 - T_1}. \tag{42c}$$

If C varies linearly with the temperature, it may easily be seen that, at the mean temperature $\frac{T_1 + T_2}{2}$, C becomes identical with the value of $[C]$ measured between T_1 and T_2.

At temperatures above room temperature this relation is fairly accurately fulfilled even in many cases where the temperature interval is large. At low temperatures, however, the variation of C with temperature often does not follow a straight-line relationship, so that Eq. (42*c*) must sometimes be taken into account when the temperature difference is only a few degrees.

The measurement of a heat content $u_{1,2}$ or a specific heat c can be made under various external conditions. In the first place, a quantity of heat q may be added to a unit weight of the substance, its volume being kept constant. In this case the term *specific heat* c_v or *molecular heat* C_v *at constant volume* is used. Experimentally, it is simpler, as a rule, to perform the heating at constant pressure, and then the *specific heat* c_p or the *molecular heat* C_p *at constant pressure* is obtained. These quantities are given by

$$C_v = \left(\frac{dQ}{dT}\right)_v \qquad C_p = \left(\frac{dQ}{dT}\right)_p . \tag{13}$$

There are certain thermodynamic relationships between C_v and C_p which will be discussed later.

As the unit for the amount of heat, the specific heat c_p of liquid water at 15°C. is generally used in physicochemical calculations, *i.e.*, that amount of heat which must be added to 1 *g.* of water at constant pressure in order to raise its temperature from 14.5 to 15.5°; this is called the *small calorie* (*cal.*). Sometimes, however, a unit 1000 times greater is more convenient, this unit being called the *large calorie* (*Cal.*) or *kilogram-calorie* (*kg.-cal.*).

b. THERMODYNAMIC AND KINETIC METHODS OF CONSIDERATION

20. General.—Similar to all other problems of theoretical physics, there exist, for the consideration of heat problems, two fundamentally different modes of treatment to which specific cases can be subjected. The first depends upon the application of very general laws (or principles) which are based upon broad empirical foundations and which are to be considered as absolutely accurate within wide limits. The results of this method are distinguished by exactness and generality. But by its use one obtains no deep insight into the concrete mechanism of the process and therefore many problems can only be solved incompletely.

The other method temporarily abandons this ground of certain knowledge and attempts to explain and to connect directly observed, special processes with the help of hypotheses and models. This procedure is characterized by probability. Its results are, of course, generally less certain than those of the former method, but the degree of uncertainty varies a great deal from case to case. An hypothesis is to be designated as relatively uncertain when it can be used only for the explanation of a single phenomenon and when a second or third hypothesis gives nearly the same result. On the other hand, if a single hypothesis interprets a large number of observable phenomena not only qualitatively but quantitatively, it is improbable that a second hypothesis could be found which would do the same. Thus, an hypothesis loses its originally doubtful character as fast as the number of phenomena which it is able to explain increases; finally, it becomes a trustworthy empirical result even though it can be approached only indirectly.

In the study of heat, the first-named method is called the thermodynamic method. It is built upon the following principles:

1. The principle of the conservation of energy (the First Law of Thermodynamics).
2. The Carnot-Clausius principle of the increase of entropy (the Second Law of Thermodynamics).
3. The Nernst Heat Theorem.

The second method is the kinetic method, which depends essentially upon the assumption that matter is built up of atoms.

Although the thermodynamic and the kinetic methods are excellent complements, it will be of advantage to keep them separated as sharply as possible in the following, on account of the fundamental differences in their principles.

α. The First Law of Thermodynamics (Energy Principle)

21. The Different Kinds of Energy.—The physical conception of energy or work is indicated most clearly by simple mechanical examples. Suppose a force $\mathfrak{K}$, such as gravity, acts upon a body. If the body is moved a small distance ds against this force, then an amount of "work" dA must be used; if it is moved in the direction of the force, then the force performs the work dA. Since this is obviously proportional to the force $\mathfrak{K}$, as well as to the distance ds, then, according to definition,

$$dA = \mathfrak{K}ds \tag{44}$$

An example of such a mechanical work, which is frequently used in the following, is given by the case where a movable piston fitted to a cylinder in which there exists a pressure p is moved against this pressure through a distance ds. If the surface of the piston (the cross-section of the cylinder) is O, then $\mathfrak{K} = p \cdot O$ and

$$dA = p \cdot Ods = pdv, \qquad (44a)$$

in which $dv = Ods$ represents the diminution of the volume of the cylinder.[1] Such work performed against a force is, of course, not lost, but is stored up in the system as **potential energy** which at any time may be given out and applied to some purpose. (*Examples:* A raised weight, a bent spring, a volume of gas compressed by means of a movable piston.)

Besides this *mechanical potential energy* there are a number of other forms of energy which may be involved in physicochemical processes:

Kinetic energy, or the energy of motion. (*Example.* A moving bullet.)

$$A = \tfrac{1}{2}mv^2. \qquad (44b)$$

Chemical Energy.—(*Example:* An explosive gas mixture before ignition.)

Electrical Energy.—The conception of an electrical field of force can be used with profit in this connection. The field of force X is understood to be that electrical force (which generally varies from point to point) which is exerted on a material point carrying a unit charge. The force $\mathfrak{K}$ on a point carrying the charge e is thus $\mathfrak{K} = Xe$. Therefore the work performed by displacing the charge e over a distance ds is

$$dA = eXds.$$

The work which must be performed by the displacement ds of a unit amount of electricity is called the **potential difference** dE between two points separated by the distance ds. Therefore, $dE = Xds$ or $X = \frac{dE}{ds}$. Now since the amount of electricity passing through any one surface (*e.g.*, the cross-section of a wire) in unit time is defined as **electric current** $i = \frac{e}{t}$, then also

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[1] If p is a known function of v, the work A which was performed over a greater volume $v_1 - v_2$ may be determined by the integration of Eq (44a). Frequently, the graphic method indicated in **10** is used for this purpose. At constant p the expression is simply $A = p(v_1 - v_2)$.

$$dA = e\,dE = i\,t\,dE. \qquad (44c)$$

Radiant or Electromagnetic Energy.—Every body at temperatures above the absolute zero sends out electromagnetic waves which fill the vacuum (luminiferous ether) surrounding the body. Radiant energy can thus be conceived of as the temporary energy (heat) content of the luminiferous ether.

Heat.—That heat also presents a form of energy follows qualitatively from the fact that heat occurs only when some other form of energy is consumed. (*Example:* The generation of heat by friction.) Quantitatively, this knowledge follows from the fact to be discussed in detail later, that heat, like the other forms of energy, completely satisfies the requirements of the First Law of Thermodynamics.

22. The Principle of the Conservation of Energy, Its Formulation and Empirical Foundation.—The principle of conservation of energy, which in the following will simply be called the energy principle, states that each of the various forms of energy may be transformed into the other forms and that this transformation takes place without either losing or gaining energy; formulated in other words: *The total energy of a closed physicochemical system always remains constant in spite of all changes which may take place within it.*

The various forms of energy are thus equivalent to each other and a definite amount of energy in one form corresponds at all times and under all conditions to an absolutely definite amount of another form. If, for instance, heat energy is transformed into mechanical energy (or conversely), according to the latest measurements 1 *Cal.* = 0.4267 *kg.-m.* The constant ratio, *mechanical energy/heat energy*, is called the **mechanical equivalent of heat.** A number of similar factors frequently used in calculation are summarized in Table 1.

In order to eliminate the trouble of transforming the various energy units, it would seem to be appropriate on the basis of the energy principle to express all forms of energy in terms of a single unit. For this purpose the *erg* (= *dyne · cm.*), which belongs to the so-called absolute system of units, is frequently used, and sometimes the electrical unit, the *joule*. At the present time, however, the units corresponding to the various forms of energy are more often used than those of a uniform system, especially in practical calculations

TABLE 1.—ENERGY UNITS[1]

	Absolute units	*Electrical units		Heat units	Mechanical units		
	Erg	Joule = watt-sec	Kw.-hr	G.-cal	L.-atmos.	Kg.-m	Hp.-hr
1 erg	1	$1 \cdot 10^{-7}$ [3]	$0.0278 \cdot 10^{-12}$	$0.0239 \cdot 10^{-6}$	$9869 \cdot 10^{-12}$	$10198 \cdot 10^{-12}$	$0.0378 \cdot 10^{-12}$
1 joule	$1 \cdot 10^{7}$ [2]	1	$0.278 \cdot 10^{-6}$	0.2390	0.009874	0.10197	$0.378 \cdot 10^{-6}$
1 *kw.-hr*	$36.0 \cdot 10^{12}$	$3.6 \cdot 10^{6}$	1	$0.8604 \cdot 10^{6}$	35550	$0.367 \cdot 10^{6}$	1.36
1 *g.-cal*	$41.863 \cdot 10^{6}$	4.1842	$1.1632 \cdot 10^{-6}$	1	0.04131	0.4267	$1.581 \cdot 10^{-6}$
1 *l.-atm*	$1013.3 \cdot 10^{6}$	101.28	$28.2 \cdot 10^{-6}$	24.205	1	10.333	$38.3 \cdot 10^{-6}$
1 *kg.-m*	$98.06 \cdot 10^{6}$	9.801	$2.72 \cdot 10^{-6}$	2.3425	0.09678	1	$3.7 \cdot 10^{-6}$
1 *hp.-hr*	$26.48 \cdot 10^{12}$	$2.65 \cdot 10^{6}$	0.7355	$0.6325 \cdot 10^{6}$	26200	$0.27 \cdot 10^{6}$	1
1 gas constant R[4]	$83.13 \cdot 10^{6}$	8.309	$2.311 \cdot 10^{-6}$	1.986	0.08204	0.8481	

[1] * Values in concordance with LANDOLT-BORNSTEIN, "Tabellen" (1923).

[2] * Exact value = $1.0005 \cdot 10^{7}$

[3] * Exact value = $0.9995 \cdot 10^{-7}$

[4] * The values of R depend upon the value selected for 0°C on the absolute or Kelvin scale and upon the molecular volume. The values in Table 1 are based upon 0°C = 273.1° abs., while throughout the text Professor Eucken uses 273.2°. In many cases rounded off values of the constants will be sufficient.

The energy principle was first clearly understood and stated by J. R. Mayer (1842), even though only with respect to the transformation of mechanical energy into heat. He also indicated a method of calculating the mechanical equivalent of heat. The principle was first tested by J. P. Joule (1840–50) by means of more exact investigations, in which mechanical work was transformed in various ways into heat. He found, as the principle demanded, that the mechanical equivalent of heat really was sufficiently constant within the limits of experimental error. As might be imagined, these limits were rather far apart at that time.

A far better proof of the correctness of the principle was given by Helmholtz in his publication in 1847, "Über die Erhaltung der Kraft."[1] Helmholtz recognized that the impossibility, which had already been demonstrated, of constructing a perpetual motion machine, *i.e.*, one which would continue running and was able to perform useful work without requiring the expenditure of energy, was nothing more than an expression of a general natural law, the energy principle. If it were possible to break this law, a *perpetuum mobile* would be an easy matter. If, for example, the mechanical equivalent of heat was not the same under all circumstances, it would be possible by suitably transforming energy in various ways back and forth between mechanical energy and heat finally to obtain energy from nothing and use this to drive a machine. On the contrary, the countless futile attempts to construct a perpetual motion machine indicated with far greater sharpness than the investigations of Joule and his successors that the heat equivalent and the other energy equivalents must be constant throughout.

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[1] Helmholtz used the word "Kraft" ("force") for the idea which today, following William Thomson's (Lord Kelvin) proposal, is characterized by the word "energy."

23. The Analytical Expression of the Energy Principle.—As a rule, thermodynamics is especially concerned with mutual transformations of the **internal energy** of bodies, of heat, and of mechanical energy. By the term "internal energy" is quite generally understood the energy stored within the body; it may be of a chemical as well as of a physical nature. In general, the internal energy U of uniform bodies is a function of both volume and temperature.

$$U = f(v, T), \tag{45}$$

in which U, as usual, refers to one mole of the substance. Only in exceptional cases, such as the ideal gases, is it dependent only on the temperature.

In Eq. (45), U represents the *absolute value* of the internal energy of a body. Experimentally, the determination of this absolute value involves considerable difficulties, but for the great majority of calculations and considerations it is not necessary to know the absolute value of the energy. It is nearly always sufficient to state the difference in the energy content of a body in two different conditions; it is, therefore, perfectly rigorous to write

$$U_1 - U_2 = f(v_1, T_1) - f(v_2, T_2).$$

Frequently, however, it is possible to write the difference $U_1 - U_2$ simply as U without being exposed to any danger of error. This simplification will be used as far as possible.

A physical or chemical process may now be considered in which the internal energy changes by dU, while simultaneously the system performs the work dA, and absorbs or liberates a certain amount of heat energy dQ.

In order to obtain an analytical expression for the energy principle which will be suitable for thermodynamics, a system may be considered which consists of (1) a large heat reservoir, such as a "calorimeter;" (2) a substance whose thermal change is to be observed; (3) an arrangement for storing up mechanical energy, *e.g.*, a cylinder fitted with a movable, weighted piston. During the investigation, the substance will suffer a certain change dU in its internal energy (chemical or thermal); a certain amount of work dA will be performed on it if necessary but at the same time a certain amount of heat dQ will be absorbed or liberated by the substance and, consequently, be liberated or absorbed by the calorimeter.

Now, if the total energy of the system is to remain constant during the investigation, then just as much energy in the form of heat dQ must be added to the system as corresponds to the increase of its internal energy dU and the work performed dA; therefore

$$dQ = dA + dU. \tag{46}$$

As an example the evaporation of a mole of H_2O at 100° may be taken. The total amount of heat dQ added in such a process is called the **total heat of evaporation**; the **internal heat of evaporation** is dU. In this case $dQ = 9710$ *cal.*, the work performed against the external pressure (see **125**), $dA = 740$ *cal.*, $dU = 8970$ *cal.* (the internal energy increases, since during the evaporation process the molecules are separated from each other and therefore work was performed against molecular attraction).

For dU there may now be written, as in Eq. (33),

$$dU = dU_1 + dU_2 = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial v}\right)_T dv.$$

If the work dA was performed merely by the change of volume pdv, then there is obtained in place of Eq. (46)

$$dQ = pdv + dU \tag{46a}$$

or

$$\frac{dQ}{dT} = \left(\frac{\partial U}{\partial T}\right)_v + \left[\left(\frac{\partial U}{\partial v}\right)_T + p\right]\frac{dv}{dT}.$$

Now, making $dv = 0$, the result is merely a heating process at constant volume (without the performance of work) and, according to Eq. (43),

$$C_v = \left(\frac{dQ}{dT}\right)_v = \left(\frac{\partial U}{\partial T}\right)_v. \tag{47}$$

If the change of volume takes place at constant pressure, $\left(\frac{dQ}{dT}\right)_p$ may be written for $\frac{dQ}{dT}$ and $\left(\frac{\partial v}{\partial T}\right)_p$ for $\frac{dv}{dT}$, and then, by applying Eqs. (43) and (47)

$$C_p - C_v = \left[\left(\frac{\partial U}{\partial v}\right)_T + p\right]\left(\frac{\partial v}{\partial T}\right)_p \tag{48}$$

is obtained.

β. The Second Law of Thermodynamics

(The Carnot-Clausius Principle)

24. The Empirical Basis of the Second Law.—While according to the First Law all forms of energy are equivalent as a matter of principle, the Second Law says that, in reality, the transformation from one form into another is not always feasible, but that the transformation, especially of heat energy into other forms, meets certain obstructions and is bound up with certain conditions. The *Second Law emphasizes the preference of certain natural processes to proceed in one direction*, while the First Law (like nearly all other physical laws) makes no statement as to the direction in which a process takes place.

A simple example will illustrate the one-sidedness of certain energy transformations. It is possible to transform any amount of mechanical (*e.g.*, potential) energy into heat by means of any of the primitive devices, such as rubbing two surfaces upon each other (the Prony brake). It is also possible to convert a certain amount of heat into mechanical energy. For example, a gas under a piston can be expanded and thus perform work whereby the gas itself becomes cooled and abstracts heat from its surroundings or a heat reservoir in contact with it. However, the expansion of the gas can take place *only once;* the amount of heat energy converted into mechanical energy is thus limited, for, in order to be able to use the gas for a new transformation of heat into mechanical energy, it must be brought back again into its former compressed state. This can be done only by reversing the entire process; the gas must again be compressed, thus expending the mechanical energy which has been obtained. It is thus shown that, by means of a finite amount of gas, no optionally large amount of heat can be taken from the surroundings and be transformed into mechanical work. This result is not by any means limited to the example chosen. It has been shown quite generally that no machine can be constructed which continues to abstract heat from its surroundings and convert it into work. Such a machine, which would naturally be of great use since the heat content of the land and ocean represents an inexhaustible supply of energy, is called a *perpetual motion of the second class. The knowledge that a perpetual motion of the second class is an impossibility forms the real empirical basis for the Second Law of Thermodynamics just as the First Law follows from the impossibility of a perpetual motion of the first class.*

25. Conditions for the Transformation of Heat into Work. (Irreversible Processes).—Even though the possibility of realizing a perpetual motion of the second class is excluded, it has not yet been stated, as the above example indicates, that a transformation of heat into work— whether single or continuous—is at all impossible, but only that in the conversion a certain condition must be fulfilled. As a closer examination of the relationships which govern these processes shows, this condition consists in the following: *The transformation of heat into work must always be bound up in a process which "of itself" proceeds in a quite definite direction.* Such processes, which are said to be **irreversible,** occur quite often in nature. The following examples may be quoted:

1. The expansion of a gas from a small volume into a larger volume (flow of a gas into a vacuum).
2. The diffusion of gases and liquids.
3. The course of a chemical reaction (explosion).
4. The flow of heat from a hotter to a colder body, etc.

Each of these processes may be utilized for the transformation of heat into work. In the above example, case 1 has already been used. In this instance it was even possible to obtain a complete, but, of course, not direct, conversion of heat into work. If it is desired to have the transformation proceed directly, generally *only a fraction of the heat* or internal (*e.g.*, chemical) energy can be set free as chemical or other forms of energy.

Now this fraction depends mainly upon the manner in which the process proceeding "of itself" or "spontaneously" is conducted. Ordinarily, *i.e.*, without a special mechanism, it will proceed so that on the whole no work will be produced. This is the case when a gas expands into a vacuum or heat flows merely by heat conduction from a hotter to a colder body. A certain useful effect is only to be obtained when the spontaneously proceeding process is controlled by means of some mechanism, and mastery of it is secured. This appliance is similar to a mountain stream, from which energy may be obtained only by damming and leading its water through a suitable canal. The useful effect actually obtained will be greater or less, depending upon the degree of elimination of losses by friction, etc., which retard the conversion. The best results are obtained when the conversion—when all losses are stopped—is made to take place infinitely slowly. Under these circumstances the process loses completely its originally violent, spontaneous character. It now no longer proceeds as an irreversible process but as a reversible one, for under the conditions described it is possible to turn the process into the one which proceeds in the opposite direction without the expenditure of appreciable amounts of energy. Of course, a truly reversible process is an ideal limiting case which is never completely realized in experiment, since small losses due to friction and other factors cannot be avoided in any practical case. *Therefore the maximum efficiency is attained in the transformation of heat into work when an irreversible process is guided into such paths that it proceeds reversibly.*

26. The Maximum Amount of Work Which Can Be Obtained by the Transformation of Heat.—The transference of heat from a hotter to a colder body may be taken as an example of how irreversible processes can be made reversible. The heat is no longer allowed to flow directly from one body to the other; the hotter body is first put into a gas, which is allowed to expand and thus absorbs a certain amount of energy; the expanded gas is then brought into contact with the colder body and thus compressed. By this means the colder body absorbs nearly (see **47**) the same amount of heat that the hotter body gave up.

Heat has, therefore, really been transferred from the hotter to the colder body, but in a quite different way from that of flowing directly from the one to the other. While originally the process was irreversible, it has now been performed reversibly, for it is easily seen that the process may also be performed in the reverse direction, whereby heat will be carried from the colder to the hotter body.

For the above process it is characteristic that, by the expansion of the gas in contact with the hotter body, a somewhat larger amount of work will be performed than must be employed for the compression of the gas in contact with the colder body. On the whole, there remains a small excess ΔA of work after the process which must correspond to the difference between the amount of heat given out by the hotter body and that absorbed by the colder. Thus, while altogether a quantity of heat Q is transferred from the hotter to the colder body, a certain fraction of it ΔQ is converted into work ΔA and

$$\Delta Q = \Delta A = Q\frac{\Delta T}{T} \qquad (49)$$

or

$$Q = T\frac{\Delta A}{\Delta T}.$$

The proof that this fundamental relation for the maximum amount of work which can be obtained from a single heat transfer is general, and is, therefore, independent of the kind of transfer mechanism employed, will be brought about by first calculating ΔA for a quite special case and then using an ideal gas as the mechanism for transferring the heat (**47**). It can then be proved that a perpetual motion of the second class could be constructed if any other formula is permissible for another reversible process. If it is assumed that for the maximum work any other equally reversible acting process held

$$\Delta A' < Q\frac{\Delta T}{T}, \qquad (49a)$$

then the first process (expansion of a gas) could be so joined to it that the *one* process extracts an amount Q of heat from the hotter body and forwards a large part of it to the colder body having an excess of work left over, while the other process works in the opposite direction and sends back exactly the same amount of heat to the hotter body.

Since the right sides of both Eqs. (49) and (49*a*) are identical, then

$$\Delta A > \Delta A' \text{ or } \Delta A - \Delta A' > 0,$$

which is the same as saying that, in spite of the fact that the hotter body has lost no heat, work has been done at the expense of the colder. Obviously, such a process can be repeated as often as desired and in this way a finite amount of energy obtained. The combination of two reversible processes in which the maximum work obtained is different in magnitude would thus permit the construction of a perpetual motion of the second class and is, therefore, to be excluded as a possibility. This possibility will be excluded if Eq. (49*a*) is rejected; Eq. (49) must thus really be valid for all reversible processes if it can be proved to be correct for only one process.

In irreversible processes the maximum amount of work is not obtained. Actually, it is found that

$$\Delta A < Q\frac{\Delta T}{T}. \tag{49b}$$

In the limiting case where the process takes place in a completely irreversible manner ΔA must be equal to zero, as has already been emphasized.

The above proof for the general validity of the fundamental Eq. (49) is remarkable in its simplicity; however, at first glance it is not quite clear how it happens that the temperature T, established in this case as a matter of definition by means of the behavior of ideal gases and introduced by means of Eq. (78), governs the relation which is valid for any substance whatever. This deficiency may be corrected in the following way: Eq. (49) may be derived without the use of a special substance, such as an ideal gas, if an undetermined but general temperature function is used instead of T. As a matter of definition, the latter is put equal to T (thermodynamic temperature scale),[1] after which it may be shown that for ideal gases Eq. (71) and, therefore, also Eqs. (73) and (78) must be valid if the Boyle-Mariotte and the second Gay-Lussac laws are considered as proved.

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[1] * This scale was developed by Lord Kelvin and is known as the Kelvin scale; accordingly temperatures may be quoted in "degrees Kelvin."

27. Maximum Work and Maximum Useful Work.—At this point the case may once more be considered in which a certain amount of internal energy is set free in a chemical or physical process. If the process is completely irreversible, the decrease in internal energy $-U$ is manifested only in the development of heat $-Q$; otherwise work $+A$ is performed in addition to the latter. In this case also the maximum value for the work A, which is usually called the **maximum work,** will be attained in completely reversible transformations; in the following this quantity will be represented by A_T. Therefore

$$-U = -Q_r + A_T, \tag{50}$$

where $-Q_r$ represents the heat liberated reversibly at the same time as A_T. The maximum work represents a very characteristic quantity for the process as a whole. As will be seen in **29,** this quantity may be absolutely determined only for processes which take place isothermally, yet this limitation is not very disturbing, since the conversion of internal energy into work is nearly always performed at constant temperature.

For the sake of clearness, it is appropriate that a concrete example should first be considered in detail. For this purpose a reversible galvanic element is suitable (for further information see **207** *et seq.*). In such an element chemical energy is partially converted into electrical energy accompanied by the absorption or liberation of a certain amount of heat. The chemical energy corresponds to the internal energy U, the electrical energy to the maximum work $A_{T,v}$ provided that besides the electrical energy no other work such as change of volume has been performed. In order to obtain an additional relation so that Q_r may be replaced by some other quantity, it will be imagined that such a galvanic cell can be used to transport heat in a reversible manner from a heat reservoir at the temperature T to another at the lower temperature $T - \Delta T$. Fundamentally, according to **26,** Eq. (49) must be strictly applicable to this case also. The process by which the heat is transported may be resolved into the following steps:

1. The element is allowed to work at the temperature T (*at constant volume*) in such a way that the electrical energy $A_e = A_{T,v}$ is generated. According to Eq. (50), the element requires

during this operation the quantity of heat $Q_r = U + A_{T,v}$, which must be taken from the hotter heat reservoir.

2. The element (at constant volume) is brought into contact with the colder reservoir at the temperature $T - \Delta T$ and adds to this an amount of heat equal to $w_k\Delta T$.

3. At the temperature $T - \Delta T$ the element undergoes a change opposite in direction to that of the first step. This requires the addition of electrical energy $A_{T,v} - \Delta A_{T,v}$. A quantity of heat will thus be added to the colder reservoir.

$$Q_r - \Delta Q_r = U - \Delta U + A_{T,v} - \Delta A_{T,v}.$$

4. The element, still at constant volume, is brought into contact with the hotter reservoir, from which it absorbs an amount of heat $w_k\Delta T$[1] and again returns to its original condition.

Since no work is performed in steps 2 and 4, the total gain of work is: $A_{T,v} - (A_{T,v} - \Delta A_{T,v}) = \Delta A_{T,v}$. A quantity of heat $Q_r + w_k\Delta T$ has thus been given to the colder reservoir. However, it is not yet permissible to apply Eq. (49), since the heat transference is not completely reversible. By reversing the cyclic process, the quantity of heat transfered from the colder to the hotter reservoir amounts to $Q_r - w_k\Delta T$. (The quantity of heat $w_k\Delta T$ always flows irreversibly in one and the same direction.)

But if ΔT is chosen vanishingly small, so that the term $w_k\Delta T$ may be neglected in comparison with Q_r, the process becomes reversible and the application of Eq. (49) is now justified. If, now, dT is written in place of ΔT, and $dA_{T,v}$ instead of $\Delta A_{T,v}$, Eq. (49) takes the following form for the present case:

$$Q_r = T\left(\frac{dA_{T,v}}{dT}\right)_v \text{ or } Q_r = T\left(\frac{\partial A_{T,v}}{\partial T}\right)_v. \qquad (51)$$

The latter expression allows the elimination of Q_r from Eq. (50), obtaining the important relation

$$A_{T,v} + U = T\left(\frac{\partial A_{T,v}}{\partial T}\right)_v. \qquad (52)$$

However, this equation has the shortcoming that it is valid only for processes which take place at constant volume, while most natural processes take place at constant pressure. In order to adapt it to the latter condition, the above cyclic process is repeated, with the difference that the galvanic element is allowed to work *at constant pressure p* and it is assumed that the heating and the cooling also take place at constant pressure. As the result of this change, the element delivers a somewhat different amount of electrical energy than before, which will be designated by $A_{T,p}$.[1] At each step of the process the volume of

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[1] The heat capacities before and after the change are not rigorously the same $\left(\text{from Eq. (211), p. 366, this difference is equal to } \frac{\Delta U}{\Delta T}\right)$, yet in the present case the difference is unimportant, since the heat quantities are eliminated in the following.

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[1] * Willard Gibbs (1873–80) called *the function* which represents the maximum work a system can perform at constant temperature and pressure, namely $-A_{T,p}$, the "*thermodynamic potential*." Helmholtz (1882) named *the function* for the maximum work at constant temperature and volume, $-A_{T,v}$, the "*free energy*." Only when the volume change is negligible, as is the case in most condensed systems, is it immaterial which of the above functions is used Unfortunately, this has led to considerable confusion in their application and at times to serious error.

* Now, constant temperature and pressure are the restraints most frequently met with in practice and most easy to produce experimentally. G N. Lewis (*J Am. Chem Soc*, **35**, 14 (1913)), or Lewis and Randall, (*loc cit*, 158)) has accordingly proposed that the thermodynamic potential should be renamed the free energy, as it is the function $-A_{T,p}$ which carries the significance of this term. This function is called the "*Maximale Nutzarbeit*" in the German edition

* In the present translation, the attempt has been made to avoid any confusion due to terminology by using the term **maximum work** and *indicating the conditions of restraint by subscripts*

* The following partial summary of the symbols commonly used is given in order to aid the student in reading the works of other authors. Care must be exercised in assigning + or − signs to these symbols, as the sign is usually a matter of definition for each case. The function $U + pv$ is often called the **heat function.** The important quantity which results from the differentiation of $A_{T,p}$ with respect to a change in chemical composition (∂m) has been variously called the *thermodynamic potential of the constituent of the mixture, the partial molal free energy* (G. N. Lewis), or the **chemical potential.** Here the latter term will be used

Function	Conditions of restraint	Gibbs	Planck	W. McC Lewis	Macdougal	G. N. Lewis	Eucken 2nd German edition	Eucken translation
$U - TS$	T, v	Ψ	F	f	F	A	$-A_T$	$-A_{T,v}$
$U - TS + pv$	T, p	ζ	ϕT	Φ	Φ	F	$-A_m$	$-A_{T,p}$
$U + pv$	T, p	χ			H	H	W	H
$\dfrac{\partial(U - TS + pv)}{\partial m}$	T, p	μ		$\dfrac{\partial\Phi}{\partial m}$	$\dfrac{\partial\Phi}{\partial m}$	$\bar{F}$		$-\bar{A}_{T,p}$

the element changes; at the first step it is v_1, at the second, v_2, etc. Then in the first step the external work performed is $p(v_2 - v_1)$; in the second, $p(v_3 - v_2)$, etc. The maximum work of the process in the first and third steps is composed of the electrical work $A_{T,p}$ and the work due to the change of volume; thus:

For the first step: $A_{T,p} + p(v_2 - v_1) = A_{T,v}$ (53)

For the third step: $A_{T,p} - \Delta A_{T,p} + p(v_4 - v_3) = A_{T,v} - \Delta A_{T,v}$.

Altogether, taking the other steps also into consideration, the result for the cyclic process is an amount of work given by

$$A_{T,p} + p(v_2 - v_1) + p(v_3 - v_2) - (A_{T,p} - \Delta A_{T,p}) + p(v_4 - v_3) + p(v_1 - v_4) = \Delta A_{T,p}.$$

The consideration which leads to the necessity of making the temperature interval ΔT and therefore also $\Delta A_{T,p}$ infinitely small remains the same as in the above. The final result is the equation

$$Q_r = T\left(\frac{dA_{T,v}}{dT}\right)_p = T\left(\frac{\partial A_{T,p}}{\partial T}\right)_p. \tag{54}$$

Before this expression is introduced into Eq. (50) it is expedient to replace $A_{T,v}$ in Eq. (50) by the left side of Eq. (53) and to introduce a new function H_p in place of U. In the present case the relation between these two quantities is defined by

$$H_p = U + p(v_2 - v_1). \tag{55}$$

Therefore, from Eqs. (50) and (54) the following is obtained:

$$A_{T,p} + H_p = T\left(\frac{\partial A_{T,p}}{\partial T}\right)_p. \tag{56}$$

The physical significance of the term $A_{T,p}$ follows directly from the example of a galvanic element used above; in this case the electric energy $A_{T,p}$ appears as the *real productive work*, while the incidental, spontaneously performed work due to change of volume (which, moreover, is generally of minor importance numerically) is quite separate from the electrical work and, in general, cannot be brought directly into use. It seems, therefore, fitting to call $A_{T,p}$ **the maximum work** of the process taking place **under constant pressure.**

The physical significance of the function H_p is obtained if the process is allowed to take place at constant pressure (generally irreversibly) in such a manner that *only* the volume work $p(v_2 - v_1)$ is performed. Then according to Eq. (46) a quantity of heat $-Q' = -[U + p(v_2 - v_1)]$ is developed. Thus, $H_p = Q'$, *i.e.*, $-H_p$ is the heat developed only during the performance of work due to change of volume at constant pressure. (*Example:* Combustion at constant pressure: $-H_p$ becomes the heat of combustion.)

If only the simple heating or cooling of a uniform substance is involved, then H_p becomes identical with the quantity Q in Eq. (43), so that

$$\left(\frac{\partial H_p}{\partial T}\right)_p = \left(\frac{dQ}{dT}\right)_p = C_p. \tag{47a}$$

It may be noted that more general thermodynamic considerations, such as will be required later, demand a somewhat broader definition of $A_{T,p}$ and H_p. Usually

$$A_{T,p} = A_{T,v} - pv \tag{53a}$$
$$H_p = U + pv. \tag{55a}$$

Thus, not only the quantities $A_{T,p}$, $A_{T,v}$, and H_p, but also U and the product pv (see **23**) represent differences between two different states of the system, *i.e.*, Eq. (53a) is merely an abbreviation of the expression (which also holds for variable pressure).

$$A_{T,p,2} - A_{T,p,1} = A_{T,v,2} - A_{T,v,1} - p_2v_2 + p_1v_1.$$

The differential Eqs. (52) and (56) do not give absolute values for $A_{T,p}$ or $A_{T,v}$ when U or H_p are given. For this purpose an integration and the evaluation of the integration constant involved are necessary. This is not possible on the basis of the First and Second laws alone, and a new fundamental hypothesis, the Nernst Heat Theorem, must be introduced. However, there are a number of important applications by which Eqs (53) and (56) may be directly tested by experiment.

28. Thermodynamic Relationships for Homogeneous Substances.— In the application of Eq. (52) to homogeneous substances, a very small but yet finite change of state is assumed. Therefore, in place of U it is more expedient to write $(\Delta U)_T$ where the index T indicates that the change takes place at constant temperature. In this case the work performed by or on the system can only be due to change of volume. Therefore, $p\Delta v$ may be put in place of $A_{T,v}$. Instead of $\left(\frac{\partial A_{T,v}}{\partial T}\right)_v$, $\left(\frac{\partial p}{\partial T}\right)_v \Delta v$ is obtained, since Δv is to be considered constant, Eq. (52) first takes the form

$$(\Delta U)_T + p\Delta v = T\left(\frac{\partial p}{\partial T}\right)_v \Delta v,$$

which, after dividing by Δv and the transformation to infinitely small changes, becomes

$$\left(\frac{\partial U}{\partial v}\right)_T + p = T\left(\frac{\partial p}{\partial T}\right)_v. \tag{57}$$

If from Eq. (55a) the quantity H_p is introduced in place of U,

$$\begin{aligned}(\Delta H_p)_T - \Delta(pv) + p\Delta v &= (\Delta H_p)_T - p\Delta v - v\Delta p + p\Delta v \\ &= (\Delta H_p)_T - v\Delta p = T\left(\frac{\partial p}{\partial T}\right)_v \Delta v\end{aligned}$$

is obtained. Dividing through by Δp, changing to infinitely small variations, and taking Eq. (34) into consideration, the result is

$$\left(\frac{\partial H_p}{\partial p}\right)_T - v = T\left(\frac{\partial p}{\partial T}\right)_v \cdot \left(\frac{\partial v}{\partial p}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_p. \tag{58}$$

Eqs. (57) and (58) form an especially convenient starting point for numerous important thermodynamic formulas for homogeneous substances. For example, Eq. (57) can be directly applied to simplifying Eq. (48) and to bring it into a more convenient form for practical purposes. If, at the same time, Eq. (34) is taken into consideration,

$$C_p - C_v = T\left(\frac{\partial p}{\partial T}\right)_v\left(\frac{\partial v}{\partial T}\right)_p = -T\frac{\left(\frac{\partial v}{\partial T}\right)_p^2}{\left(\frac{\partial v}{\partial p}\right)_T} \tag{59}$$

is obtained.

By introducing the coefficient of cubical expansion α and the volume compressibility κ it follows that

$$C_p - C_v = T\frac{v_0^2\alpha^2}{v\kappa}$$

or

$$C_p - C_v = Tv_0\frac{\alpha^2}{\kappa}, \tag{60}$$

when $\frac{v_0}{v}$ is approximately equal to 1, as in liquids and solids.

By the simple differentiation of Eqs. (57) and (58) with respect to T, the result is the frequently used formulas

$$\left(\frac{\partial\left(\frac{\partial U}{\partial v}\right)_T}{\partial T}\right)_v = \left(\frac{\partial\left(\frac{\partial U}{\partial T}\right)_v}{\partial v}\right)_T = \left(\frac{\partial C_v}{\partial v}\right)_T = T\left(\frac{\partial^2 p}{\partial T^2}\right)_v, \tag{61}$$

and introducing Eq. (47a),

$$\left(\frac{\partial\left(\frac{\partial H_p}{\partial p}\right)_T}{\partial T}\right)_p = \left(\frac{\partial\left(\frac{\partial H_p}{\partial T}\right)_p}{\partial p}\right)_T = \left(\frac{\partial C_p}{\partial p}\right)_T = -T\left(\frac{\partial^2 v}{\partial T^2}\right)_p \tag{62}$$

29. Entropy.—In the preceding paragraph it has been shown that the maximum work and maximum useful work are quantities which are characteristic for the Second Law, although they can be defined only for isothermal processes and therefore cannot embrace the whole range of phenomena governed by this law. The characteristics of irreversible processes and the transformability of heat into work which is involved in such processes can be described without any limitations by means of the conception of **entropy** (ἐντρέπειν to transform) introduced by Clausius. Due to its somewhat abstract nature, the understanding and the application of this conception generally give the student much more difficulty than the relatively clear idea of maximum work.

The common definition of the entropy S of any substance is obtained in the following equation:

$$S_2 - S_1 = \int_1^2 \frac{dU + pdv}{T}, \tag{63}$$

in which the indices 1 and 2 indicate two different states of the substance, which may be characterized by the variables p_1, v_1, T_1 and p_2, v_2, T_2 of the states.[1] Similar to the internal energy U, the entropy is generally concerned only with a difference and frequently S is written as an abbreviation for $S_2 - S_1$. The entropy, again like the internal energy, etc., is proportional to the mass of the substance, so that in the following one mole of the substance will be considered as the unit of mass. The entropy of a system consisting of several different substances is composed additively of their several individual entropies, provided no chemical change takes place. This follows directly from the equation of definition (Eq. (63)), since this additivity exists even for dU and dv.

In the following, it will be shown:

1. That S *is absolutely determined for each value of the variables which define the state, or, in mathematical terms, that* $dS = \frac{dU + pdv}{T}$ *is a complete differential.*

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[1] * The most general definition of entropy is

$$dS = \frac{dQ_r}{T}.$$

Equation (63) implies the restraint of constant pressure on the term A_T of Eq. (50). Thus, $dQ_r = dU + pdv$, since $vdp = 0$.

2. *That the change of entropy of a closed system in reversible changes of state is zero and in irreversible changes is always positive.*

The process of thinking which leads to these statements can merely be indicated in this place. For a more detailed consideration textbooks on thermodynamics must be consulted.

From Eq. (81), page 85, which on the basis of **26** holds for every simple cyclic process independent of the sort of heat-transfer mechanism used, it follows directly that

$$\frac{Q_r + dQ_r}{T + dT} = \frac{Q_r''}{T'} = \frac{Q_r}{T'}, \tag{64}$$

in which Q_r'' is the heat given out reversibly from the hotter heat reservoir or the heat taken from this by the transferring mechanism; Q_r, the amount of heat absorbed reversibly by the colder reservoir or given up by the transferring mechanism. For the sake of uniformity, putting $Q_r' = -Q_r''$, the result will be, instead of Eq. (64),

$$\frac{Q_r}{T} + \frac{Q_r'}{T'} = 0$$

Now, if $\frac{Q_r}{T} = S$, and $\frac{Q'_r}{T'} = S'$ signify the change of entropy of the heat-transferring mechanism in the first and second halves of the cyclic process, then

$$S + S' = 0, \tag{65}$$

i.e., the change of entropy of the heat carrier during the first half of the cyclic process is the reverse in sign but of the same value as that in the second half.

This result may be extended from the simple cyclic process of **27** to any more complicated cyclic process in which the carrier passes from some original state 1 through some intermediate state 2 and back again to the first. It can be shown that any complicated cyclic process can eventually be resolved into an infinite number of simpler cyclic processes by using numerous heat reservoirs so that the added amounts of heat and the individual entropy changes become very small (dQ_r or dS). Then in place of Eq. (65) the result is the sum (see, *e.g.*, CLAUSIUS, R. "Mechanische Warmetheorie," vol. 1, p. 87 *et seq.*).

$$\frac{dQ_{r1}}{T_1} + \frac{dQ_{r2}}{T_2} + \quad + \frac{dQ_{rn}}{T_n} + \frac{dQ'_{rn}}{T'_n} + \quad . + \frac{dQ'_{r1}}{T'_1}$$

$$\underset{\substack{\uparrow \\ \text{State 1}}}{=} \underbrace{dS_1 + dS_2 + \quad dS_n}_{S_{(a)}} \underset{\substack{\uparrow \\ \text{State 2}}}{+} \underbrace{dS'_n + \quad . \quad + dS'_1}_{S'_{(b)}} \underset{\substack{\uparrow \\ \text{State 1}}}{=} 0. \tag{65a}$$

Equation (65) may thus be obtained if the general statement is made that

$$S_{(a)} = (a)\int_1^2 \frac{dQ_r}{T} = (a)\int_1^2 dS, \quad S'_{(b)} = (b)\int_2^1 \frac{dQ'_r}{T} = (b)\int_2^1 dS', \qquad (66)$$

where the letters (*a*) and (*b*) indicate that the process has taken place along different paths at different times.

Considering now that the direction of the second half of the process is the reverse of that of the first half, then the sign of $S'_{(b)}$ must be changed, i.e., it is necessary to put $S'_{(b)} = -S_{(b)}$. By so doing Eq. (65*a*) takes the simple form: $S_{(a)} = S_{(b)}$. *The change of entropy is thus independent of the path* by which the substance is brought from state 1 to state 2. It follows from this that S can depend only upon the variables (p, T, v, or U) denoting the states under consideration, and is absolutely determined by these quantities. Having reached this point, it may even be assumed that the path leading to state 2 is not reversible but can also be passed over irreversibly. There remains merely to introduce the quantities dU and pdv in place of dQ in Eq. (66), doing so by means of Eq. (46*a*), and thus express the direct dependence of the entropy on the variables defining the state. In this manner Eq. (63) is again arrived at, which thus really represents an absolute definition of entropy.

The principle that the total entropy change of a closed system in reversible changes of state is always equal to zero may be found as follows: If a direct reversible energy exchange between two separate parts of the system is to be established at all, the temperatures of the two parts must be the same. If it is considered that two such parts exchanging energy always act in pairs, the result is $\frac{Q_{r1}}{T} = -\frac{Q_{r2}}{T}$ (in which heat is added to one part and withdrawn from the other) or $S_1 = -S_2$ or, finally, $S_1 + S_2 = 0$. Indeed, all parts of the system need not even have the same temperature (see, for example, the cyclic process in **26**). However, those parts of the system which have different temperatures cannot exchange energy directly but only by means of an adiabatically heated or cooled heat carrier. (In an adiabatic exchange $dQ_r = 0$ and therefore $dS = 0$.) But if for each individual isothermal exchange $S_1 + S_2 = 0$, $S_3 + S_4 = 0$, etc., the sum $S_1 + S_2 + S_3 + S_4$ must always vanish (moreover, the total entropy change of a single part of the system may be composed of several specific entropy values).

In order to prove that in any irreversible process the entropy of a closed system always increases, it is best to establish the fact first for some *special* process. As a convenient example the irreversible expansion of an ideal gas from volume v_1 to v_2 without performing work may be chosen. Since, according to **42**, $dU = 0$, it follows from **45** that the entropy difference amounts to

$$S = \int_1^2 \frac{pdv}{T} = Rln\frac{v_2}{v_1},$$

i e, it has a positive value. At present, a system will be considered which consists of any substance X, besides one mole of any ideal gas. This will be passed through a two-stage change of state: (1) The substance X undergoes an irreversible change of state, while the gas, which at present is separated from it, remains unchanged. (2) The substance is brought back to its original state by means of a reversible process. Now, an irreversible process can be made retrograde only when at the same time some other substance will undergo an energy change In the present case this change may consist in an addition of heat to the ideal gas [1] This heat will be used to perform an isothermal, reversible expansion of the gas, thus increasing its volume. The expansion of the ideal gas is then used to compress the gas X back to its original volume v_1. The final state of the system is, therefore, distinguished by X having returned to its original state while the ideal gas occupies a greater volume than before, the entropy of the system has thus increased But this increase cannot result from the second step, since here only reversible changes were performed It must therefore be ascribed to the first step, the irreversible change in X

For systems in which, besides work due to volume change, still other kinds of work (such as electrical work) are performed, then, instead of the special Eq (46*a*), the more general Eq (46) is used and the result is

$$dS = \frac{dQ_r}{T} = \frac{dU + dA}{T} \text{ or } dA = TdS - dU \tag{67}$$

Since this equation deals exclusively with reversible processes, A obviously represents a maximum value of the work performed, yet A is not absolutely defined by Eq (67), since it is not like S and U in being dependent only on the limiting values of the variables which define the states, but depends also on the path over which the process was conducted (dA is an incomplete differential). As an example showing that A really depends on the path, a chemical reaction which begins at one temperature T_1, and ends at another T_2 may be considered. The reaction can at one time be performed isothermally at the temperature T_1 while performing the work A_1 and the system then be brought from T_1 to T_2. Another time the system could first be warmed to T_2 and the reaction then allowed to proceed, performing the work A_2. Since no work was performed in the changing of temperature, in the two processes two amounts of work A_1 and A_2, were obtained, which, in general, are not the same

[1] For example, if the irreversible process consists in a direct transference of the heat quantity Q_2 from a warmer to a colder substance, then a total amount of heat $Q_1 - Q_2$ must be added to the gas by means of which Q_2 (through a reversal of the cyclic process described in **47**) is to be again "pumped up."

The relations will be simplified if only isothermal processes are considered and the discussion thus limited merely to establish the conception of maximum work for such processes, as has already been done in the above

Since in this case T is now to be considered as a constant, a complete differential is obtained instead of Eq (67): $dA_{T,v} = d(TS - U)$, so that the maximum work obtained in a transition from state 1 to state 2 is now absolutely defined by

$$A_{T,v_2} - A_{T,v_1} = (TS_2 - U_2) - (TS_1 - U_1) \quad \text{or,} \quad \text{abbreviated,}$$

$$A_{T,v} = TS - U. \tag{67a}$$[1]

By combining Eqs (53a) and (67a), the result is

$$dA_{T,p} = d(TS - U) - d(pv) \tag{67b}$$

or

$$-dA_{T,p} = d(U - TS) + d(pv)$$

It is obvious that $A_{T,v}$ and $A_{T,p}$ can be defined by means of $A_{T,v} = F(T, v)$ and $A_{T,p} = F'(T, p)$ The partial differential forms for these are

$$dA_{T,v} = \left(\frac{\partial A_{T,v}}{\partial v}\right)_T dv + \left(\frac{\partial A_{T,v}}{\partial T}\right)_v dT \tag{A}$$

$$dA_{T,p} = \left(\frac{\partial A_{T,p}}{\partial p}\right)_T dp + \left(\frac{\partial A_{T,p}}{\partial T}\right)_p dT \tag{B}$$

From Eqs (67a) and (67b)

$$-dA_{T,v} = dU - TdS - SdT$$

and

$$-dA_{T,p} = dU - TdS - SdT + pdv + vdp,$$

and by applying Eq (50)

$$-dA_{T,v} = -pdv - SdT \tag{C}$$

$$-dA_{T,p} = vdp - SdT. \tag{D}$$

By comparing the coefficients of dv, dp, and dT in Eq (A) and (C), and (B) and (D) the following important relations result

$$S = \left(\frac{\partial A_{T,v}}{\partial T}\right)_v = \left(\frac{\partial A_{T,p}}{\partial T}\right)_p \tag{67c}$$

$$\left(\frac{\partial A_{T,v}}{\partial v}\right)_T = p; \left(\frac{\partial A_{T,p}}{\partial p}\right)_T = -v \tag{67d}$$

* Various attempts have been made to make the conception of entropy clearer. Some physicists (e g, see GOODENOUGH, *loc cit*, pp 51, 66) divide energy into two classes, available energy and unavailable energy. Entropy is a measure of the latter. TOLMAN (*Phys. Rev.*, **9**, 244 (1917)) considers entropy as a quantitative measure of the "run-downness" of the system. The two ideas are obviously related. J. Willard Gibbs evidently considered entropy as a measure of the "mixed-upness" of the system, although his ideas on this subject were not published. Boltzmann considered entropy as the degree of "disorder" of the system and approached the subject from the standpoint of probability; this view will be discussed later in **33.**

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[1] * The remainder of **29** has been taken essentially from the first edition.

30. Equilibrium Conditions.—In the above it has been emphasized as a characteristic of reversible processes that they could be conducted in either direction without requiring an especially large expenditure of energy, *i.e.*, the smallest impulse is sufficient to cause the process to change its direction. Conversely, a system existing in such a state has of itself no motive to change direction; it persists continuously in its original state for the same reason that a ball lying on a perfectly plane plate has no motive to put itself into motion even though only a very slight impulse is sufficient to do so. *A system engaged in an infinitely slow, reversible transformation is therefore in equilibrium at every point.*

The result arrived at in this way is: when the system satisfies the conditions of a reversible transformation, then at the same time the conditions for (thermal) equilibrium are also fulfilled. *A general criterion for equilibrium is therefore given by the principle that in a reversible process the entropy change of the total system is zero.* Limiting the method to isothermal processes—and this is permissible for the following—then the maximum work may again be used in place of entropy. As has already been emphasized, the maximum work will always be produced when the process is conducted reversibly; conversely, a reversible process is dealt with whenever the work actually performed A is equal to the maximum work $A_{T,v}$. The condition of equilibrium is thus

$$A = A_{T,v}.$$

Now frequently a work due to change of volume $A = \int pdv$ enters into the problem as the only work performed. If the special case of a process taking place at *constant volume* is considered, then $dv = 0$ throughout the entire process, and therefore $A = 0$. It thus follows for the condition of equilibrium that

$$A_{T,v} = 0. \qquad (68)$$

In an isothermal process taking place under *constant pressure* have $A = pv$ and therefore

$$A_{T,v} = pv \quad \text{or} \quad A_{T,v} - pv = A_{T,p} = 0, \qquad (68a)$$

i.e., a system which is kept under constant pressure will be in equilibrium when it is able to perform no useful work.

Concerning the direction in which a system not in equilibrium will change spontaneously (irreversibly), the following may be said: as it has been shown above, work can be obtained from heat or internal energy only when it is bound up with a process which takes place irreversibly and spontaneously; the converse of this law states that if in any process work is obtained from heat or internal energy then this process originally was one which proceeded spontaneously. Therefore, a system changes spontaneously into the direction in which (by conducting the process reversibly) it performs work, *i.e.*, in which $A_{T,v}$ or $A_{T,p}$ is positive. If secondary influences are disregarded, the tendency of a system towards a transformation will obviously be greater the greater its ability to perform work. This conception is especially important for chemical processes; according to van't Hoff, the maximum work is a direct, exact measure for the tendency of substances to react with each other, or, in other words, a measure of the "chemical affinity" which for a long time had been but a vague idea.

(γ) Fundamentals of Kinetic Theory

31. Fundamental Assumptions.—The older kinetic theory of heat was based upon the following three assumptions:

1. Matter is composed of the smallest particles—atoms or molecules—all of which are absolutely the same in a homogeneous substance.
2. Heat energy consists in the mechanical energy of molecules.
3. The mechanical laws established by macroscopic experiments and astronomical observations are valid for molecules.

32. The Atomic Hypothesis.—The first of these assumptions involves the atomic hypothesis. Certain Greek Philosophers (Lucretius and Democritus about 500 B.C.) took up the question of whether matter was infinitely divisible, arriving finally at the conception that the divisibility must end at some point—just as at that time there was believed to be a limit to the universe. They called these small particles atoms (*ἄτομος* = the indivisible). For more than two thousand years the problem advanced no further, and therefore it remained as a vague hypothesis.

An exact basis (in the present sense of the term) for this conception was first obtained by the discovery of the fundamental chemical law of constant and multiple proportions (Dalton, 1808), according to which certain fundamental substances (elements) always combined with each other in quite definite ratios by weight. Without doubt the simplest explanation of this law consisted in imagining that the elements were composed of small particles (atoms) which were exactly the same for each element and which always combined in quite definite numbers to form a chemical compound (molecule). It was not a very great step to consider that in purely physical processes these molecules were the real building stones of all matter. Even though several further qualitative arguments were added in favor of this conception, it retained for a long time the character of a pure but not improbable hypothesis but at first was by no means generally accepted by science.

A revolution in scientific opinion set in only after the discovery of a number of new, to a large extent physical, phenomena which allowed the hypothesis to be approached from a quantitative standpoint and which enabled investigators to calculate the exact weight of the individual atoms and molecules. The determination of the weight of a single molecule resulted in the calculation of a number which represented the number of molecules **N** actually contained in one mole of the substance. This number is called **Avogadro's number.**[1]

As long as Avogadro's number could be calculated only by means of rather inexact methods, the result was scarcely a proof of the atomic hypothesis. In the last twenty years, however, a number of exact and completely independent methods of determining **N** have been developed, the results of which are summarized in Table 2.

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[1] * Avogadro (1811) advanced the hypothesis that equal volumes of all gases at equal pressures and temperatures contain the same number of molecules (see **40**). Thus, Avogadro's name became associated with the *number of molecules per mole.* The first to indicate a way to estimate the magnitude of this quantity was the Viennese physicist, Loschmidt (1865), and in many German books on physics and chemistry this number is referred to as "Loschmidt's number." Some books (*e g*, ANDRADE, "Structure of the Atom," London (1923)) use Loschmidt's number for the number of molecules *per cubic centimeter* of substance. Here the term "Avogadro's number" with the symbol **N** will be used for the number of molecules per mole.

TABLE 2.—VALUES OF AVOGADRO'S NUMBER **N** DETERMINED BY VARIOUS METHODS

No	Method	Discoverer of method	$N \cdot 10^{-22}$ from the more recent measurements	Source of data upon which calculation was made	Source of further information
1	Kinetic theory of gases	Loschmidt, 1865, improved by Sutherland, 1893	59 5 to 68	EUCKEN, *Physik Zeit*, **14**, 324 (1913)	BYK, A, "Kinetische Gastheorie," Jahnke, Leipzig
2	Brownian movement				
	a Distribution of particles in a gravitational field	Perrin, 1909	60 9	WESTGREN, *Arkiv Mat Svensk Vet Akad*, **13**, No 14 (1918)	**152** this book
	b Change of position of particles	Einstein, 1905	59 1	NORDLUND, *Z Physik Chem*, **87**, 40	**154**
	(1) Solid and liquid particles		60 3	FLETSCHER, *Phys Rev*, **4**, 440 (1914)	
			60 4	EYRING, *Phys Rev*, **5**, 412 (1915)	
	* (2) Bacteria		60 8	SHAXBY, *Proc Roy Soc*, **104A**, 655 (1923)	
3	Law of black-body radiation	Planck, 1900	60 5	GERLACH, *Z Physik*, **2**, 76 (1920) WARBURG and MULLER, *Ann Physik*, **48**, 410 (1917)	**340**
4	Determination of the charge of an electron				
	a. Cloud droplets	Townsend, 1897, improved by Millikan, 1910	60 62	MILLIKAN, *Physik Zeit*, **14**, 796 (1913), *Phil Mag* (6), **34**, 1 (1917)	**268**
	b α-particles	Regener, 1909	60 4	REGENER, *Berl Akad Ber*, **1909**, 948	**280**
5	Scattering of the light from heavenly bodies by the atmosphere.	Lord Rayleigh, 1899	60 4	FOWLER, *Astrophys J*, **40**, 435 (1914)	**155**
			64 5	DEMBER, *Ann Physik*, **49**, 599 (1916)	
6	Fine structure of spectral lines	Sommerfeld, 1916	60 8	PASCHEN, *Ann Physik*, **50**, 901 (1916)	LADENBURG, R *Jahrb Radioakt und Elektronik*, **17**, 93 (1920)

The most probable value at the present time is **N** $= 6.06 \cdot 10^{23}$. The remarkable quantitative agreement of the values of **N** from the most widely differing methods would be quite inconceivable if they were not all concerned with a common fact. The results given in Table 2 thus form the real empirical basis for the atomic theory; the assertion that atoms and molecules are actually present in matter is no longer an hypothesis but a principle firmly established by experience.

33. Motion Due to Heat.—That the molecules in the gaseous and liquid states can be conceived as being continuously in motion is made very probable by the fact that two different gases or liquids in contact with each other will in the course of time become completely mixed of their own accord (diffuse into each other). Since by means of a diffusion process the molecules undergo a change of position in spite of the fact that they have not been stirred or otherwise put into motion by outside means, it follows that they must spontaneously perform motions of their own.

It might, however, be imagined that in diffusion the particles move towards and mix with each other due to their attractive forces. It would then be necessary to assume that at the termination of the diffusion the motion ceases. But it can be shown that in many cases no force of attraction acts between the particles and yet diffusion takes place. It follows that the motion of the particles, made apparent by the process of diffusion, must itself be quite independent of diffusion and therefore does not cease when diffusion ceases. *Thus the molecules of the gaseous and liquid states must exist in continuous rapid motion.*

In solid substances which resist any change of outward form (distortion, etc.) it must be assumed that the molecules do not move freely as in gases and liquids, but are bound to certain positions of rest. In spite of this, however, they are by no means immovable, but perform rapid though very small vibrations about their positions of rest or, more exactly, their positions of equilibrium.

Although the motions of the individual molecules, whether they be in gaseous, liquid, or solid state, are generally invisible, they correspond to a certain amount of mechanical energy. In the simplest case of gases at low concentrations this energy is mostly kinetic; in other cases, such as solids, potential energy is also involved. There can be no doubt that this mechanical energy of the molecules must form a part of the internal energy of the substance.

The kinetic theory makes the special assumption that the mechanical energy of the individual molecules is identical with the heat energy, *i.e.*, with the part of the internal energy which varies with temperature $\int_{1}^{T_2}\left(\frac{\partial U}{\partial T}\right)_v dT = \int_{T_1}^{T_2} C_v dT$. On this hypothesis is built the present bold attempt to unite thermodynamics and mechanics, two branches of physics which are apparently quite dissimilar. This attempt, however, immediately meets with theoretical difficulties which consist mainly in that in thermodynamics a kind of process (irreversible process) is met with which is entirely foreign to mechanics, or, what amounts to the same thing, a radical difference exists between heat energy and other forms of energy.

The classical investigation of Boltzmann has shown that such a distinction between heat and other forms of energy is not wholly justified. It is only necessary to consider that a fundamental difference exists between the ordinary mechanical-kinetic energy of a substance and the kinetic energy of its molecules: In the first case, in the macroscopic, mechanical motion of a body, an *ordered* motion is involved—all parts of the body have the same components of motion—but the second case involves motion which is *completely disordered in respect to magnitude as well as direction.*

Considered from this viewpoint, the Second Law states that the ordered motion can change directly into disordered, the degree of "disorder" usually increasing spontaneously—the increase of disorder is, therefore, characteristic of irreversible processes, similar to the increase of entropy—but an ordered motion cannot be directly obtained from a disordered one. The quantitative treatment of the problem required a combination of mechanical principles with theoretical, probability (statistical) considerations, and thus gave rise to the new subject of "statistical mechanics." The most important result of this consists in a fundamental formula for entropy,

$$S = k \ln w + Const.,$$

in which the entropy appears as a simple function of the *probability w* of the state of the system and thus obtains a clear physical meaning. It is evident that a system will endeavor to reach the state of greatest "probability" and therefore, after some time, disregarding minor deviations, will adjust itself at a point of maximum probability. The characteristic of entropy, that it always increases in irreversible processes, is thus explained by statistical-mechanical considerations.

In simple cases, such as in ideal gases, the probability of a state can be exactly formulated and be evaluated numerically.[1]

34. The Law of Distribution of Velocities.—In developing the kinetic theory of heat, it was first attempted to apply the fundamental principles of the ordinary mechanics to molecules; for example, molecules were considered as rigid elastic spheres which collided with each other like billiard balls and thus exchanged direction and magnitude of motion. According to another conception, molecules were considered as force centers mutually influencing each other like the heavenly bodies. An absolutely exact, purely mechanical solution of the problem for any optional moment of time cannot possibly be calculated in advance on the basis of one of these conceptions of the motions and velocities of all molecules, since this involves "the problem of n-bodies" and "the problem of 3-bodies" is not yet solved.

However, by means of statistical considerations a considerable simplification can be obtained, so that the calculations can be carried out and yield tangible results. The procedure, of course, works in a rather arbitrary fashion and leads only to a statement as to the average behavior of a large number of molecules, yet such a result is nearly always sufficient, since, as a rule, the average effect of a large number of molecules is what is actually measured by experiment. If it is desired to follow the path of a single molecule (**153**) it is only possible to make a statement of the probability of the molecule, *i.e.*, one can state the degree of probability that it will show a certain behavior—for example, that it will travel a definite distance in 1 sec., etc.

One of the most important results of such calculations is Maxwell's law of the distribution of velocities. This law indicates how many molecules of a gas at any determined instant possess a certain velocity or are contained within a definite velocity interval. For example, the following table expresses the results obtained for oxygen at 273.2° *abs.*:

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[1] For further information see LEWIS and RANDALL, *loc. cit.*, chap. XI; SCHAEFER, *loc. cit.*, chaps. IX and X.

TABLE 3.—DISTRIBUTION OF VELOCITIES FOR OXYGEN AT 273.2° ACCORDING TO MAXWELL'S LAW

Velocity interval (ΔV), meters per second	Number of particles $\left(\frac{\Delta N}{N_0}\right)$, per cent
Below 100	1 4
100–200	8 1
200–300	16 7
300–400	21 5
400–500	20 3
500–600	15 1
600–700	9 2
Above 700	7 7

If the calculation of the molecules is repeated for another instant, the same result will always be obtained, disregarding trifling deviations, so that, even if the velocities of individual molecules increase or decrease, the average number of molecules within a definite velocity interval remains unchanged, since at all times approximately as many molecules leave the velocity interval as enter it.

If the velocity interval is restricted to 1 *m.* instead of 100 *m.*, as in Table 3, then the law of distribution of velocities can be represented graphically as a smooth curve (Fig. 13), where the abscissa represents the velocity in meters per second and the ordinate the percentage of molecules contained in a velocity interval 1 *m.* wide (*e.g.*, between 300 and 301 *m.*).

It is seen that molecules with very great and very small velocities occur but seldom; half of all the molecules at 273° have velocities between 300 and 553 *m.*, the most frequently occurring velocity being 376.6 *m.* Concerning any particular single molecule, as has been mentioned before, only the following sort of probability statement can be made: The probability that the velocity of the molecule falls between 300 and 553 *m.*

is 0.5, the probability that it falls between 300 and 301 *m* is 0.002, that it falls between 700 and 701 *m*. is 0.00065.

The complete formula for the distribution law is

$$\frac{dN}{N_0} = \sqrt{\frac{2}{\pi}}\left(\frac{M}{RT}\right)^{\frac{3}{2}} e^{-\frac{MV^2}{2RT}}\, V^2\, dV, \tag{69}$$

in which $\frac{dN}{N_0}$ signifies that fraction of all the molecules N_0 the velocities of which lie within the intervals V and $V + dV$.

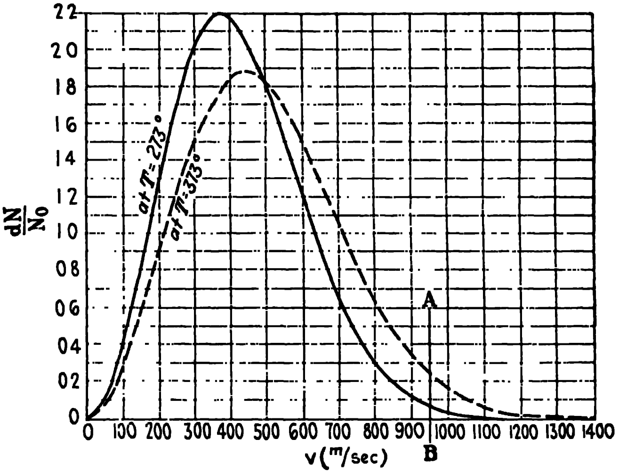

FIG. 13

If only *one component* of velocity V is considered, such as V_x, then in place of Eq. (69) the following simpler function is obtained:

$$\frac{dN}{N_0} = \sqrt{\frac{M}{2\pi RT}}\, e^{-\frac{MV_x^2}{2RT}}\, dV_x, \tag{69a}$$

for which the general course, like that of Eq. (37), is illustrated by Fig. 12.

35. The Law of Distribution of Energy.—Very closely related to the distribution of velocities is the *distribution of the kinetic energy of molecules*. However, the energy distribution of the individual molecules of a uniform gas will not be considered—the solution of this is given directly by Eq. (69)—but the behavior of the average energy of the molecules in different gases will be examined. Then, if the energy values of the individual molecules, similar to the velocities, deviate much from each other and change continuously, the average kinetic energy of a single molecule, *i. e.*, the arithmetic mean of the energy values of all the individual molecules, possesses a quite definite value, which can be calculated from statistical mechanical principles.

The result of the lengthy calculation involved in this is extremely simple and perhaps is clear without much explanation. On the average, the kinetic energy of the molecules is completely compensated. *If two gases are in thermal equilibrium with each other, then the mean kinetic energies of their molecules are equal.*

In this simple statement the result is, of course, only true for gases in which the total energy consists entirely of the energy of translatory motion. It is, therefore, assumed that the molecules do not rotate nor do the atoms within the molecule vibrate with respect to each other. The magnitude and the direction of the total velocity of such molecules, and thus their total state of motion, are obviously determined by the magnitudes of the three velocity components u, v, and w in the directions of the three space coordinates. But the state of motion of more complicated molecules is not fixed by the velocity components u, v, w of its center of gravity alone; the rotation of the whole molecule and the vibration of the atoms with respect to each other must also be considered. In order to represent these motions, more coordinates are required.

For the complete reproduction of the motion of a body of any shape, such as a cylinder with an oval cross-section, it is, for example, necessary to have three determinative quantities, since three angles are required to fix the position of the cylinder in space—two (the latitude and the longitude) to determine the position of the cylinder axis, and one to determine the degree of rotation of the body about its own axis.

According to Maxwell, each such determinative quantity is called a "degree of freedom";[1] a point and a perfectly spherical body thus each has three degrees of freedom, an ellipsoid, 3 + 3 = 6 degrees of freedom, etc.

[1] * This term, as used in this connection, must, of course, not be confused with its meaning in the chemist's "phase rule."

The general law of equipartition of energy states: *The energy of an optionally shaped molecule in the state of equilibrium is equally divided among the degrees of freedom, i.e.,*

$$\text{the energy in any one degree of freedom} = \frac{\text{total energy of the molecule}}{\text{number of degrees of freedom}}.$$

36. The Necessity of an Extension of the Classical Mechanics for Its Use in Molecular Processes.—The kinetic theory, which is based upon the three assumptions quoted in **31**, leads in many cases to complete success, *i.e.*, it really permits a number of thermal and related properties of matter to be correctly calculated qualitatively and quantitatively. The kinetic theory of gases in particular has led to many beautiful results. For example, the principle predicted from it that the internal friction and the ability to conduct heat must be very nearly independent of the density was very satisfactorily confirmed by experiment. The specific heat of gases also shows in many cases a behavior which agrees well with classical theory. However, observations which directly contradicted the theory have not been lacking at any time. In particular, it does not seem at all possible to confirm the law of equipartition of energy for every case. In order to find a way out of this difficulty, it was first assumed that, in those cases which disagreed with the law, equilibrium was interfered with or was attained with exceeding slowness. No experimental proof for the correctness of this assumption could be produced, however. Moreover, since in more recent times the contradictions, especially of the equipartition law, have become more and more frequent, the conviction was finally reached that a supplementary hypothesis, such as the above assumption that equilibrium was reached only very slowly, was not sufficient and more radical treatment was necessary. Of the three fundamental assumptions of **31**, the first two are to be considered unconditionally as quite certain; the only way out of the difficulty therefore lies in changing the third. In this way, it was finally conceived that another sort of mechanics was involved in molecular process; the new laws must, of course, also apply to macroscopic bodies and transform into the ordinary mechanical laws as a limiting case.

Simple, but quite new, laws have already been found for a number of molecular and atomic processes which cannot be classified according to the classical mechanics (compare **294** *et seq.*). These new laws are distinguished by the presence of a universal constant h, called *Planck's constant of action*, which plays an important part in all of them and which is entirely foreign to the classical mechanics. To be sure, a general theory embracing molecular and atomic as well as macroscopic phenomena is only in the stage of development.

2. IDEAL GASES

a. Empirical Foundations

37. The Ideal Gas as a Limiting State.—The majority of natural phenomena which present themselves directly to the senses are rather complex and therefore may, at least theoretically, be resolved into simpler phenomena. One of the main tasks of the physicist often consists in uncovering and describing these simple fundamental phenomena. Sometimes such a resolution can be performed only by theoretical treatment, but frequently experimental means are useful, especially when the conditions of investigation are suitably chosen, in bringing forth clearly the basic phenomenon which is to be studied, and in repressing disturbing secondary phenomena.

For example, if the equation of state of a gas were investigated, *i.e.*, the dependence of its volume on the pressure and temperature, the result would be rather complicated if the investigation were carried out at high pressure and low temperatures. The results, however, become simpler and more uniform (the various gases become more and more similar in their behavior) if low pressures and high temperatures are chosen. It is thus quite natural to consider the state of a gas at a vanishingly low pressure as a limiting state to which all gases consistently strive and which yields a pure fundamental phenomenon free from all disturbing factors. A gas existing in this state is usually called an **ideal gas.**

Sometimes experiments can be conducted at pressures where the deviations from the ideal state of a gas practically vanish.

But if, for any reason, it is necessary to work at higher pressures, then experiments must be performed at several pressures (*e.g.*, 1 and ½ *atm.*) in order to find the deviation from the ideal state. From the difference between the two results the probable behavior of the gas at zero pressure can be determined very accurately. (This extrapolation to the ideal state is considered in greater detail in **96.**)

The following section is concerned exclusively with the ideal gases. It will be assumed that the investigations used to illustrate the laws of this state were performed either under the conditions of the ideal gaseous state or the extrapolation of the results to vanishingly small pressures has already been made. It may be noted, however, that the discoverers of the gas laws did not know of this extrapolation.

38. The Laws of Boyle and Mariotte and Gay-Lussac.—The English physicist, Boyle (1664), and the French chemist, Mariotte (1676), independently investigated the compressibility of gases at constant temperature. They found the well-known law:

$$pv = p_0v_0 = Const. \tag{70}$$

Considerably later Gay-Lussac (1802) investigated the temperature dependence of the volume at constant pressure and the pressure at constant volume, finding that

$$v = v_0\left(1 + \frac{1}{273.2}T_c\right) = \frac{v_0T}{273.2}. \tag{71}$$

This equation is identical with Eq. (39) in **18,** and therefore does not represent an independent connection between gas volume and temperature, but is merely a definition of the ordinary temperature scale. The volume change which is to be expected when temperature and pressure change is given by uniting Eqs. (71) and (70), so that

for a change of temperature: $v'_0 = \frac{v_0T}{273.2}$;

for a change of pressure: $pv = p_0v'_0 = \frac{p_0v_0T}{273.2}$. (72)

If the two changes are considered as taking place one after th other, the result must naturally be the same as when both tak place at the same time For the change of pressure at constant volume ($v = v_0$), then directly from Eq. (72) is obtained:

$$p = \frac{p_0 T}{273.2},$$

i.e., the change of pressure of a gas at constant volume is the same as the change of volume at constant pressure.

39. The General Gas Law.—Equations (70), (71), and (72) hold for any definite amount of gas; v_0 thus signifies the volume of the gas at 273.2° *abs.* and at the pressure p_0; correspondingly, v is the volume at the temperature T and pressure p.

It is especially convenient to choose the same value of v_0 for all gases. If this is done, the expression

$$\frac{p_0 v_0}{273.2} = R$$

becomes a universal constant, if the unit for expressing the term p_0 can be agreed upon.

On the basis of a principle advanced by Avogadro (1811), which will be discussed in the following paragraph, in a volume v_0 at a definite temperature (*e.g.*, 273.2°) and under a definite pressure p_0 there is always a definite number of molecules or moles which is independent of the kind of gas enclosed. When it has thus been established that a mole of any one ideal gas at 273.2° and $p_0 = 1$ *atm.* occupies the volume $v_0 = 22.41$ *l.*, then one mole of any other gas under the same conditions will occupy the volume $v_0 = 22.41$ *l.*

If Eq. (72) is always referred to one mole, then for all gases

$$pv_m = RT \tag{73}$$

For a quantity of gas containing n moles, it follows directly that

$$pv = nRT \tag{73a}$$

if $v = nv_m$ is the volume containing n moles. Further, if, in place of the number of moles n, the weight G and the molecular weight $M\left(n = \frac{G}{M}\right)$ are introduced, then

$$pv = \frac{GRT}{M}. \tag{73b}$$

According to Eq. (73), the **gas constant** R assumes the following values:[1]

$$R = \frac{1 \times 22.41}{273.2} = 0.0821 \ l\text{-}atm.$$

$$\frac{760 \times 22.410}{273.2} = 62{,}396 \ mm.\ \mathrm{Hg} \times cubic\ centimeters$$

$$\frac{760 \times 13.596 \times 22.410}{273.2} = 8.314 \times 10^7 \ ergs,$$

depending upon the units used in measuring the pressure and the volume; 1 *atm.* = 760 *mm.* Hg = 76 × 13.596 *g.* per square centimeter = 76 × 13.586 × 980.6 *dynes* per square centimeter and v is measured in liters or cubic centimeters. In many calculations it is also convenient to use R in calorimetric units; thus (see also Table 1),

$$R = \frac{8.315 \times 10^7}{4.19 \times 10^7} = 1.986 \ cal.$$

40. Avogadro's Law.—The principle advanced by Avogadro is not based upon physical considerations but upon the simple chemical fact that in reactions between gases a whole-number relationship between the gas volumes is involved (Gay-Lussac-Humboldt law, 1805). But the principle cannot be derived wholly from this, as may be easily shown by the following example:

In the formation of water it is observed that 1 *l.* of oxygen unites with 2 *l.* of hydrogen to form 2 *l.* of water vapor. If the molecular weights and formulas are not known, as was still the case in Avogadro's time, then one would first try to write the equation for the formation of water in the form

$$\mathrm{O} + \mathrm{H} = \mathrm{HO}.$$

With respect to the volume relations, this form would signify that 1 *l.* of oxygen has twice as many atoms as 1 *l.* of hydrogen or water vapor. On the other hand, the form $1\mathrm{O}_2 + 2\mathrm{H}_2 = 2\mathrm{H}_2\mathrm{O}$, in view of the fact that 1 *l.* O_2 + 2 *l.* H_2 = 2 *l.* $\mathrm{H}_2\mathrm{O}$, signifies that every liter in each one of the three gases contains the same number of molecules. Since the molecular weights were unknown at the time, it was not possible to know whether to write O or O_2 for gaseous oxygen, and it follows, therefore, that the numbers of molecules contained in a definite volume of the various gases were either the same *or* were related to each other in the ratio of simple whole numbers. By a bold stroke, Avogadro removed the "or" and simply postulated that *the number of molecules contained in a definite volume under the same conditions of temperature and pressure is the same for all gases.*[1]

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[1] If T is considered as dimensionless (see also p. 37, second footnote), then R represents an energy quantity.

Thus at first Avogadro's principle was only an hypothesis. In the course of time it became fundamental for the development of important chemical conceptions (see **57**). In the beginning, however, it met with powerful opposition, since numerous investigators at that time still tacitly considered all elementary gases as monoatomic and in such cases the ideas of atomic and molecular weight were not to be distinguished from each other.

41. Dalton's Law.—If various gases all under the same pressure p and occupying the volumes v_1, v_2, v_3 . . are brought into contact by removing the partitions which separate them, they will be completely mixed after a time without the pressure p having changed. Since each gas now fills the entire volume $v = v_1 + v_2 + v_3$ . . . , each must exist under a lower pressure than before. The pressure of each gas in a mixture of gases is called its **partial pressure** (p_1, p_2, p_3 . . .). According to the above experimental result, the sum of the partial pressures is always equal to the total pressure (Dalton, about 1800). This law may be directly obtained mathematically if Eq. (70) is applied to each single gas.

$$\begin{aligned} pv_1 &= p_1v \\ pv_2 &= p_2v \\ pv_3 &= p_3v \\ p(v_1 + v_2 + v_3 \quad\quad) &= v(p_1 + p_2 + p_3 \quad . \; . \;). \end{aligned}$$

Since $v = v_1 + v_2 + v_3$

it follows that

$$p = p_1 + p_2 + p_3 \; . \; . \; . \tag{74}$$

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[1] See footnote to **32**.

At the beginning, it could be doubted whether it was permissible to apply Boyle's law to the mixture of gases. However, the fact that the total pressure does not change during the mixing confirms Eq. (74) and the assumption upon which it is founded that two gases can be mixed without Boyle's law losing its validity.

Moreover, the partial pressure of a gas can be experimentally demonstrated when a wall or partition which is permeable to the one gas but not to the other is available. Glowing platinum is fairly permeable to hydrogen but not so to other gases. The gas which the semipermeable partition allows to pass through always attempts to equalize its partial pressure on both sides of the membrane; if, for example, a glowing platinum bulb is filled with air at 1 *atm.* pressure and is then put into hydrogen also at 1 *atm.*, the hydrogen will flow into the bulb until its partial pressure inside the bulb is 1 *atm.*, the total pressure within the bulb thus having increased to 2 *atm.*

42. The Second Law of Gay-Lussac.—Gay-Lussac allowed a gas enclosed in a vessel to flow into an evacuated vessel and established the fact that, on the whole, neither heating nor cooling occurred in this process. The internal energy of an ideal gas thus remains unchanged by increase of volume, *i.e.*, the internal energy of a gas at constant temperature is independent of the volume, so that

$$\left(\frac{\partial U}{\partial v}\right)_T = 0, \tag{75}$$

which is the mathematical statement of Gay-Lussac's second law.

43. The Molecular Heat.—A summary of the experimentally determined values of the molecular heat of a number of gases at constant volume C_v and the dependence of these values on the temperature is contained in Table 4. Column 4 of this table shows for which temperatures the given value of C_v holds. Column 5 contains the percentage change of this value with temperature, $100\,\frac{1}{C_v}\frac{dC_v}{dT}$, at room temperature. The last column contains certain values $\left(\frac{k}{h\nu}\right)$ characteristic for the change of C_v at high temperatures and which become smaller as the temperature variation decreases. These values will be discussed in **75.**

TABLE 4.—MOLECULAR HEATS (C_v) OF GASES

Group	Gas	C_v	Temperature, degrees absolute	Temperature coefficient at room temperature, in per cent	$\frac{k}{h\nu}$ Eq. (98a), 74
1	Hg	2.98	550–630		Vanishingly small
	K, Na	3.0	1000–1300		
	He	2.98	90–290	Null	
	A	2.98	90–3000	Null	
	Ne, Kr, Xe	3.0	290		
2	H_2	1.87	290	Very small	$\frac{1}{5000}$
	N_2, O_2	4.96	90–290		$\frac{1}{4100}$
	CO	5.00	90–290		
	HCl	5.00	290		$\frac{1}{4100}$
	Cl_2	5.86	290	0.085	$\frac{1}{930}$
3	H_2O	6.15	373	0.027	$\frac{k}{h\nu_1} = \frac{1}{2500}$ $\frac{k}{h\nu_2} = \frac{k}{h\nu_3} = \frac{1}{5000}$
	CO_2	6.87	290	0.140	$\frac{k}{h\nu_1} = \frac{1}{980}$ $\frac{k}{h\nu_2} = \frac{k}{h\nu_3} = \frac{1}{2300}$
	N_2O	7.17	290	0.16	
	CH_4	6.50	290	0.13	
	NH_3	6.67	290	0.055	
4	C_2H_2	8.38	290	0.25	
	C_2H_4	8.16	290	0.25	
	C_2H_6	10.30	290	0.30	
	C_6H_6	23.3	350	0.35 (350°)	

From this table it is seen that the gases may be divided into groups according to their molecular heats:

1. The molecular heat is about 3 *cal.* and is apparently quite independent of the temperature. These are the gases which from their behavior in other respects are said to be monoatomic.

2. The molecular heat at room temperature is very nearly 5 *cal.* The variation of C_v around room temperature is slight, but increases gradually towards higher temperatures. These are diatomic gases. Chlorine, which is likewise diatomic (as well as the other halogens), shows an irregular behavior.

3. Triatomic gases and certain others with four and five atoms. C_v is between 6 and 7 *cal.* and even at room temperature

increases considerably more with increasing temperature than for gases of group 2.

4. This group cannot be sharply distinguished from group 3. C'_v is greater than 7 *cal.* and on the whole increases in greater amounts as the number of atoms in the molecule increases. The temperature coefficient increases with the molecular heat.

b. THERMODYNAMIC RELATIONS

44. The Difference: $C_p - C_v$.—Since the internal energy of any homogeneous substance is a function of the temperature and pressure (Eq. 45), then for small changes of U (see Eq. (33))

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT + \left(\frac{\partial U}{\partial v}\right)_T dv$$

Now $\left(\frac{\partial U}{\partial T}\right)_v$ may be designated by C'_v, then $\left(\frac{\partial U}{\partial v}\right)_T$ becomes zero on the basis of the second law of Gay-Lussac (Eq. (75)) and it follows, therefore, that

$$dU = \left(\frac{\partial U}{\partial T}\right)_v dT = C'_v dT \tag{76}$$

If the heating takes place at constant pressure, then from Eq. (43)

$$C'_p = \left(\frac{\partial Q}{\partial T}\right)_p = \frac{dU + pdv}{dT} = C'_v + p\left(\frac{\partial v}{\partial T}\right)_p.$$

But according to the gas law (Eq. (73))

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p},$$

which results in the important relation

$$C'_p - C'_v = R = 1.986 \text{ cal.} \tag{77}$$

if the molecular heat is expressed in the usual heat units (calories).

If $C'_p - C'_v$ is experimentally determined in calories, and the constant R, in agreement with its original definition, is expressed in mechanical units, such as *ergs*, then Eq. (77) gives a method for determining the mechanical equivalent of heat The first calculation of this fundamental constant was made according to this method by the discoverer of the energy principle, R. J Mayer.

45. The Work Performed in Isothermal, Reversible Processes. The work performed by an infinitely small change of volume against the pressure p is always $dA = p\,dv$. However, the pressure generally changes also during the performance of a finite amount of work; therefore p must first be expressed as a function of v and thus an integration will be involved. If, as the result of Eq. (73), one puts

$$p = \frac{RT}{v},$$

which means that

$$dA = RT\frac{dv}{v}$$

for a finite amount of work performed at constant temperature, then, by integrating,

$$A = RT\,ln\,v + Const.$$

or

$$A_{1,2} = RT\,ln\frac{v_2}{v_1}, \qquad (78)$$

where $A_{1,2}$ is the amount of work which is performed by the expansion of a gas from v_1 to v_2. In place of the volume, the pressure can also be introduced according to Eq. (70), obtaining

$$A_{1,2} = RT\,ln\frac{p_1}{p_2}. \qquad (78a)$$

Therefore, the work performed by an isothermal process depends *only* on the ratio of the initial and the final volumes (or pressures). For example, in an expansion from 200 to 100 *atm.*, the work performed is the same as that in the expansion from $^1/_{50}$ to $^1/_{100}$ *atm.*

46. Adiabatic Changes.—If a pressure or volume change of a gas takes place in such a way that the heat generated or lost during the compression or expansion is retained[1] in the gas, the result is that form of change of state which is called **adiabatic.** The quantity dQ in Eq. (46) thus disappears, and

$$dQ = dU + dA = 0 \quad \text{or} \quad dA = -dU,$$

---

[1] Experimentally, this is attained with quite sufficient approximation if the compression or expansion is performed *rapidly*. In order completely to retain the heat in the gas during a slow compression, the walls of the containing vessel would have to be completely impenetrable to heat, a condition which experimentally is never quite satisfactorily fulfilled.

i.e., the work performed is equal to the decrease of internal energy. Taking Eqs. (76) and (73) into consideration,

$$C_v dT = -p\,dv = -RT\frac{dv}{v}, \tag{79}$$

which when integrated, assuming C_v constant, gives

$$C_v\,ln\,T = -R\,ln\,v + Const.$$

From Eq. (77), by introducing $\frac{C_p}{C_v} = \gamma$, the result is

$$ln\,T + (\gamma - 1)\,ln\,v = Const.$$

and finally

$$Tv^{\gamma-1} = Const. \tag{80}$$

In order to obtain a relation which is analogous to Boyle's law T is eliminated by means of Eq. (73) and

$$pv^{\gamma} = Const. \tag{80a}$$

obtained. A comparison of this formula with that of the Boyle-Mariotte law (Eq. (70)) shows that in an adiabatic compression the pressure is greater than for an isothermal compression, since γ is always greater than unity.

The adiabatic processes offer various possibilities for determining C_v or C_p experimentally. Working only with small temperature changes, it is convenient to use Eq. (79) directly, *i.e.*, the gas is allowed to expand through a definitely determined volume dv against a definite pressure and the resulting temperature change is measured either directly or indirectly.

47. The Maximum Efficiency Obtained by the Transformation of Heat into Work. The Carnot Cycle.—In the reasoning which led to the fundamental Eq. (49), **26** still lacks one thing, namely, the proof that for the special case of a machine driven by an ideal gas the maximum useful work which can be obtained amounts to $\frac{Q\Delta T}{T}$. This deficiency can now be removed by means of Eqs. (78) and (80*a*) and the application of a cyclic process first suggested by Carnot (1824). By the help of these, heat will be transferred reversibly from a container at the temperature $T + \Delta T$ to one at the lower temperature T.

In the warmer container a mole of an ideal gas will be allowed to expand *isothermally* and *reversibly* (*i.e.*, very slowly) from the volume v_1 to v_2 (Fig. 11). According to Eq. (78), the work performed in this process is $R(T + \Delta T)\ ln \frac{v_2}{v_1}$ and an equivalent amount of heat Q_1 is withdrawn from the container. The gas is then expanded adiabatically (likewise reversibly, but very rapidly in order to avoid losing heat), so that the gas is cooled to the temperature T. The work performed in this case must correspond directly to that of cooling the gas, and is therefore $C_v\Delta T$. The volume is now v_3. The gas is brought into contact with the colder container and is compressed isothermally to the

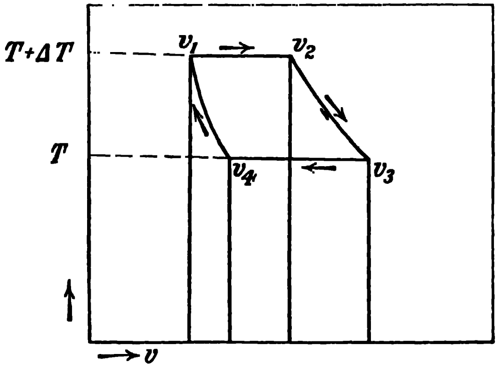

FIG. 11

volume v_4. The external work performed upon the gas, which is equivalent to the amount of heat Q_2 added to the colder container, is $RT\ ln \frac{v_3}{v_4}$. The volume v_4 is so chosen that by an adiabatic compression corresponding to ΔT exactly the original volume v_1 is reached. The energy required for this last step of the process is again $C_v\Delta T$. Since the energy for the heating and cooling directly compensate for each other (each amounts to $C_v\Delta T$), there is obtained by this cyclic process a quantity of work given by

$$\Delta A = R(T + \Delta T)\ ln \frac{v_2}{v_1} - RT\ ln \frac{v_3}{v_4}$$

But from Eq. (80), which must hold for this case,

$$\frac{v_3}{v_2} = \left(\frac{T + \Delta T}{T}\right)^{\frac{1}{\gamma - 1}} = \frac{v_4}{v_1}.$$

Hence it follows that

$$\frac{v_2}{v_1} = \frac{v_3}{v_4}$$

and thus for ΔA it is found that $\Delta A = R\Delta T \, ln \frac{v_2}{v_1}$.

Now, since

$$Q_1 = R(T + \Delta T) \, ln \frac{v_2}{v_1} \quad \text{and} \quad Q_2 = RT \, ln \frac{v_2}{v_1},$$

the useful effect of the process, *i.e.*, the ratio of the work performed to the heat transferred, is, as has already been assumed in **26**:

$$\frac{\Delta A}{Q_1} = \frac{\Delta T}{T + \Delta T} \quad \text{or} \quad \frac{\Delta A}{Q_2} = \frac{\Delta T}{T}, \tag{81}$$

depending on whether ΔA is compared with the heat given out by the warmer container Q_1 or with that absorbed by the colder container Q_2.

c. KINETIC THEORY

48. The Kinetic Derivation of the Gas Laws.—As the simplicity and the generality of the gas law would suggest, the fundamental assumptions of the kinetic theory developed in **31** are quite sufficient to explain it on a purely kinetic basis without the addition of special supplementary hypotheses.

Qualitatively, the pressure exerted by a gas follows directly from the kinetic conception of what constitutes a gas. If the gas consists of a large number of rapidly moving molecules flying about in complete disorder (Boltzmann fittingly compares the molecules of a gas to a swarm of gnats), then these molecules must strike the walls of the containing vessel from time to time and be compelled to turn back. The walls, therefore, continuously receive impulses from impinging molecules, similar to a target being hit by bullets, and would be moved if not firmly fixed in place. In order to keep the walls in their places, a certain opposing force, *i.e.*, a certain pressure, must be applied to each unit area of the surface to compensate for the effect of the molecular impacts. It is thus possible to consider the total effect of the molecular impacts as a pressure acting outwardly and in the following this pressure will be referred to as the **thermal pressure.**

The quantitative calculation of the thermal pressure from kinetic data involves no difficulties, provided some simplifying assumptions are introduced.

Consider a cubic gas container of exactly 1-*cc.* volume. The number of molecules contained in it will be $N = \frac{\mathbf{N}}{v_m}$. Now consider that the irregular motion of the molecules is somewhat changed, so that the molecules move only at right angles to the six walls of the cube.[1] Then only one-sixth of all the molecules $\left(\frac{N}{6}\right)$ will move towards one wall. The number which strikes the wall during a very small interval of time dt is found as follows: If schematically the same velocity $[v]$ is assigned to all the molecules, then during the time dt only those molecules will reach a wall which previously were at a maximum distance of $dx = [v]\,dt$ from it.

The total number of molecules N' which strikes the wall during the time dt is thus equal to the number which was contained within a prism with the base of 1 $cm.^2$ and height $dx = [v]\,dt$ and therefore the volume of $[v]\,dt$. Thus for N'

$$N' = \frac{N}{6}[v]\,dt$$

By the collision of a single molecule with a wall, the latter receives an impulse amounting to $2m\,[v]$; if the molecule remained at rest after its collision, it would impart an impulse of only $m\,[v]$ to the wall, but, since on the average it travels away[2] from the wall with the velocity $-[v]$, the wall receives another impulse of $m\,[v]$, or, altogether, $2m\,[v]$. In the time dt, one wall with a surface of 1 $cm.^2$ will receive impulse to the amount of

$$2m[v]N' = \frac{Nm[v]^2dt}{3}.$$

Therefore, during the time dt the wall, which has a mass m', would undergo the impulse $m'd[v] = \frac{Nm[v]^2dt}{3}$. This can be compensated by a pressure or force[1] p, since it can be written (from Eq. (13)) $m'd[V] = pdt$. From this it follows that the pressure on the walls of the vessel must be

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[1] Boltzmann has given a rigorous proof for the authorization of this simplifying assumption

[2] Obviously, for such motion to continue the molecules must be considered as being "perfectly elastic."

$$p = \frac{mN[V]^2}{3} = \frac{m\mathbf{N}[V]^2}{3v_m} \tag{82}$$

or, if there is a volume v containing n moles,

$$pv = \frac{nm\mathbf{N}[V]^2}{3} = \frac{nM[V]^2}{3}, \tag{82a}$$

since $nm\mathbf{N} = Mn$ represents the mass of all the molecules. According to Maxwell's equipartition law (**34**) the individual molecules cannot in any way be considered to possess equal velocities and therefore $[V]$ in Eq. (82) does not represent a definite velocity, but $[V]^2$ represents a mean value called the *root-mean-square-velocity*, generally written $\overline{V^2}$.[2]

Since p, v, n, and M can be assumed to be known, the term $\sqrt{V^2}$ can be determined without difficulty by means of Eq. (82a); for H_2 it amounts to 1838 *m./sec.*, for N_2, 492 *m./sec.*; for O_2, 461 *m./sec.*; for Cl_2, 310 *m./sec.*; for I_2, 164 *m./sec.* at 273.2° *abs.*

It will suffice here to show that the quantity $\sqrt{V^2}$ is not at all the same as the mean velocity $\overline{V}$, indeed, it is greater than $\overline{V}$, since in the first case the larger velocities have a greater effect on the determination of the mean (due to taking the squares) than in the ordinary "average." In the same way the velocity V_m, which corresponds to the maximum of the curve of Fig. 13, is different from both $\overline{V}$ and $\sqrt{V^2}$, and, in general, the result is

$$V_m = \frac{\sqrt{\pi}}{2}\overline{V} = \sqrt{\frac{2}{3}\overline{V^2}} \tag{82b}$$

49. Avogadro's Law as the Result of the Law of Energy Partition.—If various gases with molecular weights M_1, M_2 . . . and root-mean-square-velocities V_1^2, V_2^2 . . . are put into containers of equal volume v and under the same pressure p, it follows from Eqs. (82*a*) or (80)

$$pv = \frac{n_1M_1V_1^2}{3} = \frac{n_2M_2V_2^2}{3} = \quad .$$

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[1] Force and pressure are the same in this case, since a force per unit area is involved.

[2] * This is equal to the sum of the squares of the velocities of all the particles divided by their number (see LEWIS, W. McC., A System of Physical Chemistry, London (1921) vol. **1**, p. 2).

or

$$pv = \frac{N_1 m_1 \overline{V_1^2}}{3} = \frac{N_2 m_2 \overline{V_2^2}}{3} = \cdot \quad ,$$

where N_1, N_2 . . . are the numbers of molecules of the first, second, etc. gases contained in the volume v. But the fundamental energy partition law, which can be derived from purely mechanical considerations (see **35**), states that the mean kinetic energy L of the individual molecules must be the same for all, therefore $L_1 = L_2 = L_3$ or

$$\tfrac{1}{2} m_1 V_1^2 = \tfrac{1}{2} m_2 V_2^2 =$$

must be true. Therefore, *Avogadro's law* $N_1 = N_2 = N_3$ *follows as a simple result of the kinetic method of treatment and especially of the energy partition law.*

50. The Absolute Temperature.—If Eq. (81) is compared with Eq. (73), which refers to one mole of substance, it is found that

$$pv_m = RT = \frac{MV^2}{3}$$

$$T = \frac{M}{R}\frac{V^2}{3} = \frac{2}{3}\frac{L_{mol}}{R} \tag{83}$$

The absolute temperature is therefore proportional to the mean kinetic energy $\overline{L}$ of the molecules of an ideal gas and can be used as a direct measure of it. In this way the idea of temperature becomes very simple. In particular, the existence of an "absolute zero" becomes understandable, since at this point the kinetic energy will have decreased to its lowest possible value, zero; negative values for this magnitude are to be excluded, since $\overline{L}$ must always be positive.

51. The Second Gay-Lussac Law.—The second Gay-Lussac law (see **42**) follows directly from the fundamental assumptions of the kinetic theory of ideal gases. Since no force exists between the molecules except at the moment of collision, no work is performed when they are moved closer together or farther apart. The total energy of a gas is thus independent of the position of the molecules. It consists simply in the sum of the energies (predominantly kinetic) of the individual molecules, and is therefore not a function of the volume. Formally speaking, the internal energy does not depend upon the volume because kinetic consideratons give U as the function of the temperature alone.

52. The Molecular Heat. If there are gases for which the internal energy U consists only in the kinetic energy of molecular motion in straight lines, then the internal energy U per mole must be simply

$$U = \overline{L} = \tfrac{1}{2}M\overline{v^2} = \tfrac{3}{2}RT \qquad (84)$$

and the molecular heat (for all temperatures) is

$$C_v = \tfrac{3}{2}R = 2.98 \ cal. \qquad (85)$$

Since the translatory motion takes place in three degrees of freedom (see **35**), then, according to Eq. (84) and the energy partition law, each degree of freedom must correspond to an energy

$$U = \tfrac{1}{2}RT$$

and a molecular heat

$$C_v = \tfrac{1}{2}R = 0.993 \ cal$$

To these three degrees of freedom, which are always present in translatory motion, there must be added, for theoretical purposes, two further degrees of freedom of rotational motion if the molecule can be considered as a rotating body, to describe the position of the symmetry axes and thus the whole body, two angle-coordinates (latitude and longitude) are required. Such a molecule must have a molecular heat of $C_v = \tfrac{3}{2}R + \tfrac{2}{2}R = 4.97$ *cal.* Three degrees of freedom of rotation, and therefore a molecular heat of 6 *cal.*, must be assigned to an optionally shaped molecule without a symmetry axis, since three angles are necessary to define its position in space. On the other hand, an increase of only one in the number of degrees of freedom and thus a gas with a molecular heat $C_v = 3.97$ *cal.* cannot be conceived. Besides the extreme case of three degrees of freedom of rotation, a *vibrational motion due to the mutual displacement of the atoms within the molecule* also gives rise to degrees of freedom, the maximum number of which for Z atoms is: $Z - 1 + Z - 2 + Z - 3 = 3Z - 6$. As will be explained in greater detail when solid substances are considered from the kinetic standpoint (see **67**), potential energy also occurs in such a vibration, and the energy of such a degree of freedom is therefore nearly twice as great as for a purely kinetic degree of freedom.

As the maximum value for the atomic heat of a gas with Z atoms per molecule ($Z > 2$) the result is

$$C_v = {}^3\!/_2R + {}^3\!/_2R + (3Z - 6)R. \qquad (86)$$

As Table 4 shows, Eq. (85) is quite accurately fulfilled by a number of gases which are usually considered as monoatomic. This indicates that there really are gases in which the internal energy consists entirely of translatory motion. In the sense of the existing theory, it must be concluded that in these molecules other degrees of freedom (*e g.*, rotation) are not present and that the molecules are to be regarded either as real point centers of force or as rigid, elastic, quite smooth spheres, because for the determination of the position of a point or a sphere three space coordinates are sufficient. More recently, however, the view has been upheld that rotational and other degrees of freedom could also be present even in the monoatomic gases but that, similar to the rotational degrees of freedom of the H_2 molecule, they were not able to absorb energy at low temperatures (compare below).

The next group in Table 4, which consists entirely of diatomic gases, has a molecular heat of nearly 5 *cal.*, while gases which within a large temperature interval have molecular heats of 4 *cal.* are lacking. According to the present theory, this means that the diatomic molecules must be considered as rotating bodies. This agrees very well with the early conception of atoms as spheres, since two spheres joined to each other like a dumb-bell do, indeed, represent a body which can rotate. Even among the diatomic gases, however, the theory is not so well satisfied as by the monoatomic gases, the absolute value of C_v deviates quite considerably (*e.g*, chlorine) from the theoretical value and at high temperatures C_v has a temperature coefficient which is unexplainable on the above theory. The values for the remaining gases are still less in agreement with the theory.

For some of the three- and five-atom gases the molecular heat, indeed, lies in the neighborhood of 6 *cal.*, as the theory requires for molecules without symmetry axes and without vibrational energy within the molecule, yet in the molecules containing larger numbers of atoms the excess of the molecular heat above the theoretical value is considerable. But this excess above the value $C_v = 6$ *cal.* can now be reconciled with the theory; it means that molecules with several atoms, even in the case of diatomic molecules, contain a certain amount of vibrational energy within the molecule.

It is a fact, however, that the law of energy partition does not explain why the molecular heat should change continuously with the temperature, since according to Eq. (86) it should change only in amounts equal to whole numbers times $\frac{R}{2}$ Therefore, nothing remains but to assume that the degrees of freedom of internal vibration gradually appear as the temperature increases. This behavior of the intramolecular energy of vibration gives us the first concrete example of the failure of the classical kinetic theory, which has already been referred to in **36.**

As a matter of principle, the rotational energy behaves similarly. The deviations from the classical theory can certainly be shown directly in one case, hydrogen. Even at room temperature the molecular heat of hydrogen is distinctly *below* the normal of 4.98 *cal.* and decreases gradually as the temperature becomes lower to the value of 2.98 *cal.*, the characteristic value for monoatomic gases. This low value is attained by hydrogen at the temperature of 60° *abs.* Just as the degrees of freedom of internal vibration gradually develop at high temperatures, the rotational motion disappears towards the lower temperatures. For this also, the classical theory is unable to give any explanation.

Only for the monoatomic gases, which involve only the kinetic energy of translatory motion, is the classical theory quite definitely established, as far as is known at present. Moreover, if the energy of straight-line, translatory motion should nevertheless "degenerate" similar to the rotational energy at low temperatures, then not only deviations from the classical value of C_v but also from the gas law $pv_m = RT$ at low temperatures must be shown, since the magnitude of the thermal pressure depends directly upon the energy of translatory motion. Such deviations have not yet been observed with certainty. Therefore, a failure of the existing mechanics has not yet been experimentally demonstrated for the straight-line motion of molecules. Yet theoretical considerations have been advanced according to which such a "degeneration" of monoatomic ideal gases is probable, but, of course, only at the lowest temperatures, which experimentally cannot be attained because of the condensation of all gases.

53. The Mean Free Path.—In the kinetic derivation of the gas law and the considerations concerning the energy content and molecular heat of ideal gases, concrete statements regarding the path over which a single gas molecule passed were unnecessary. In a number of other thermal properties, physical as well as chemical, this is no longer the case.

A molecule, at every collision with another molecule, undergoes a sudden change of direction and therefore on the whole describes a zigzag path. The short, straight portions of this path are called the *free paths*, but these are, of course, not at all equal in length; at times the distance traveled between two collisions will be very short and at other times quite long. But if the mean value of a large number of the free paths is taken, then the resulting **mean free path** l, the average length of all the small straight-line sections in the path of the molecule, will still represent a quantity which is characteristic of the gas. If the gas is expanded, the individual sections of the zigzag, and therefore the mean free path, become larger; if compressed, they become smaller and a calculation shows that the mean free path is inversely proportional to the density. Instead of the mean free path, the course of the molecule can be characterized by the number (Z) of collisions which it undergoes in 1 *sec.* Since the average distance traversed by the molecule *in 1 sec.* is $\bar{v}$, then $\bar{v} = l \cdot Z$.

Among the properties which are dependent upon the mean free path we have the diffusion coefficient, the heat conductivity, and the coefficient of internal friction. Conversely, from the experimentally determined value of one of these constants it is possible to calculate the mean free path. For air under normal pressure in this way it is found that $l = 0.95 \times 10^{-5}$ *cm*, but, at a pressure of $^1/_{1000}$ *mm.* of Hg, l is nearly 10 *cm.* Thus, if the molecules under these latter conditions were placed in a cubic vessel with each edge measuring 10 *cm.* (volume = 1 *l.*), then, in general, a molecule could move from one wall to the other without encountering another molecule on the way.

d. APPLICATIONS

54. The Importance of the Gas Laws in Theoretical Problems. The principal importance of the general gas law

$$pv_m = RT$$

in theoretical problems lies mainly in the fact that the ideal state of a gas is completely governed by theory and furthermore that it permits a transition to more complex and difficult problems, thus frequently revealing a way to their solution. An example of this is given by Eq. (49) for the maximum useful effect obtained in the transformation of heat into mechanical work. This equation is, indeed, generally valid on the basis of general experience (the impossibility of a perpetual motion of the second class); but the path which led to it involved considerations in which an ideal gas played a decisive part.

55. Temperature Measurements by Means of Gas Thermometers.—Since the ordinary temperature scale is defined by the gas law, in exact temperature measurements it is always necessary to refer back to the gas laws, especially in the standardization of thermometers and for the establishment of the "fixed points" used in thermometry. For this purpose a gas thermometer is generally used in which the volume and molar content of gas is fixed and known, and the pressure is variable and adjustable. The gas thermometer at constant pressure is less seldom used; in this case the pressure and the volume are given and the number of moles of gas is variable and adjustable. In exact temperature measurements by means of the gas thermometer, just as in the exact determination of the molecular weight (of gas), the deviation from the ideal gas must be carefully taken into account. A hydrogen thermometer filled at 0°C. and 1000 *mm.* pressure is $\frac{5}{100}°$ too high at $-193°$; at higher temperatures the deviations are considerably less.[1]

The gas law is of further practical importance for the direct measurement of gas temperatures, especially if these vary rapidly (as in gas explosions) and it is possible to measure the pressure by a rapidly operating, registering manometer. The method is capable of various applications. For example, if the amount of heat Q liberated by the explosion is known, then from this and the temperature of the explosion, as determined by the gas law from the measured pressure, it is possible to calculate the heat content of the gas mixture after the explosion and thus the mean specific heat of gases up to very high temperatures. This method, first used by LeChatelier and A. Langen, was developed by M. Pier into a precision method, to which the present knowledge of the specific heat of gases between 2000 and 3000° *abs.* is due.

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[1] The exact measurement of temperature by means of the gas thermometer is discussed in greater detail by HENNING, "Temperaturmessung," Braunschweig (1915).

The gas thermometer method of measuring temperatures is also applicable to the determination of the heating which occurs during an adiabatic compression and which leads to a calculation of C_v according to Eq. (79) (the method of Clement and Desormes). Since this case does not involve a determination of the absolute temperatures, but only small temperature differences, the method can be carried out by means of relatively simple equipment.

56. The Determination of Molecular Weight on the Basis of the Gas Law.—In Eq. (73*b*) five quantities occur besides the universal gas constant R. These quantities are pressure, volume, temperature, the weight of the gas, and the molecular weight.

Since the conditions may be so chosen that the first four can be easily measured experimentally, the gas law gives an excellent method for the determination of the "molecular weight" M of a substance in the gaseous state.

Concerning this point, it may be shown in particular that, in the sense of the gas law, the molecular weight, which can be fittingly designated as the **physical molecular weight,** is not necessarily identical with the chemical molecular weight. The physical molecular weight M, as is shown most clearly by kinetic considerations, is defined by $M = \mathbf{N}m$, where m is the *mean weight of the smallest particles which still move about freely in the gas, the "physical molecule."* How these particles are constructed, whether they are held together by physical or chemical forces, is immaterial in this definition. In this sense, for example, a tiny dust particle visible to the naked eye is a physical molecule. By a **chemical molecule** is generally understood the smallest uniform aggregate of atoms held together by chemical forces. It is to be borne in mind, therefore, *in the application of the gas laws that the molecular weight thus found does not need to be identical with the chemical molecular weight.* Of course, in many cases the two are actually the same.

Numerous experimental methods exist for the determination of the molecular weight by the help of the gas laws and these methods may be summarized most simply by noting which quantities in Eq. (73*b*)—pressure, volume, temperature, amount of substance—are fixed at the beginning by the experimental conditions (in the mathematical sense, these are the independent variables) and which one is determined during the investigation (the dependent variable). In this way the following summary is obtained:

Fixed by the experimental conditions	Determined	The method was developed by
T, p, v	G	Dumas, 1827, for vapors Regnault, 1847, for gases
T, p, G	v	Viktor Meyer, 1878
G, T, v	p	Blackmann, 1908, Menzies, 1911.
T, G	p and v	Gay-Lussac Hofmann, 1868

57. Atomic Weight Determination.—The atomic weight of an element is generally determined by means of some chemical compound in which the element is combined with another of known atomic weight. Obviously, such a determination is possible only when the chemical formula of the compound concerned, *i e*, the valence of both elements is known.

One of the most important methods for determining chemical formulas depends upon Avogadro's law. On account of its shortness, it will be described as a simple example.

Suppose the problem is to determine the formula of water. Investigation shows that

$$22.41\ l.\ \text{oxygen} + 44\ 82\ l.\ \text{hydrogen} = 44\ 82\ l.\ \text{water vapor.}$$

If it is assumed that the physical and the chemical molecules are identical in this case, then the equation for the reaction must read

$$1O_n + 2H_m = 2H_mO_{\frac{1}{2}n}.$$

Since the number of atoms of each element in a chemical molecule must be at least 1, then n must be at least 2. Concerning m, nothing can be said directly and it may, for example, be equal to 1. This would mean that hydrogen is a monoatomic gas and must have the same valence as oxygen. Water would then have the formula HO and be diatomic. Now the number of atoms in the compound can be inferred from the molecular heat (compare Table 4 and **52**), but, of course, the most extreme case to which this method can be applied is that of triatomic molecules, and even among the diatomic molecules it is not quite certain in its results. Hydrogen would be correctly considered as diatomic from its molecular heat measured at room temperature, but monoatomic from that at low temperatures (see **52**). From purely chemical considerations, however, a satisfactory result is obtained if other reactions are also studied. Putting, as in the above, $1H_m + 1Cl_p = 2H_{\frac{1}{2}m}Cl_{p\frac{1}{2}}$ for the formation of hydrogen chloride or $3H_m + N_q = 2N_{\frac{1}{2}q}H_{\frac{3}{2}m}$ for the formation of ammonia, it is seen that $m = p = q$ must be at least 2. If no reaction can be found in which $n > 2$ and $m > 2$, then $n = m = 2$ is the correct value and the formula H_2O for water is established with certainty.

Thus, in general, the method is not able to establish beyond doubt an equation for a reaction nor the chemical formula of the compound from the observed reaction alone, but it succeeds in doing so if other reactions in which the same element or compound occurs are taken into consideration. Even though this method, based upon Avogadro's law, is scarcely needed in modern times for the determination of the number of atoms in a molecule, it was of greatest importance in the development of chemistry as the basis of all atomic weight determinations.

3. IDEAL AND SIMPLE SOLID SUBSTANCES

a. Empirical Foundations

58. The Ideal Solid Substance. (Limiting State).—The counterpart of the ideal gas is the **ideal solid.** As the ideal gas is the limiting state of matter at high temperatures and low pressures, so is the ideal solid the limiting state at low temperatures and high pressures.

The properties of the ideal solid substance in the limiting state are extremely simple: All mechanical and thermal properties are independent of the temperature; volume, compressibility, and heat content have a constant value, and therefore the coefficient of thermal expansion and the temperature coefficient of compressibility and of specific heat have the value zero.

Experimentally, it is very much more difficult to approximate the ideal state for solid substances than the ideal gas; the pressures required are enormously greater and probably must be reckoned in terms of millions of atmospheres if the substance is to be brought anywhere near this limiting state at room temperatures. It is more effective and practical to reduce the temperatures; in the immediate neighborhood of the absolute zero, matter transforms to the ideal limiting state, even at vanishingly low pressures.

Since, as far as is known at present, the absolute zero cannot be reached experimentally,[1] the possibility of realizing the absolutely ideal limiting state is excluded, at least as far as finite pressures are concerned. However, it is worth mentioning that in many cases the deviations from the ideal state, even at higher temperatures and lower pressures, are so small that they cannot be determined with the accuracy of measurement now attainable. As Nernst has shown experimentally, the atomic heat of diamond between 20 and 60° *abs.* is already equal to zero within the limits of experimental error. Most other substances first reach the region in which the deviations from the ideal state become vanishingly small at somewhat lower temperatures than the diamond. Now while there are no measurements in this region, it may be clearly seen from the behavior of the temperature curve of the volume and heat content found at higher temperatures that these quantities reach practically constant values even at finite temperatures. An example of this is given

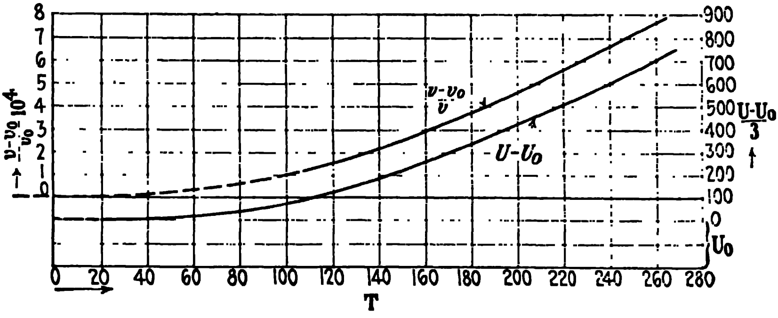

FIG 15

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[1] * H. Kamerlingh Onnes reports having reached a temperature of slightly below 1° *abs.* with liquid helium (*Trans. Faraday Soc.*, **18**, Part 2 (Dec., 1922)).

in Fig. 15, which represents the dependence of the volume and the internal energy upon the temperature for the case of fluorite.

59. Ideal Solid Substances. (Transition State).—Even above the range where solid substances exist in a really ideal state and their thermal properties are independent of the temperature, solid substances follow quite simple and general laws; therefore, the term "ideal solid substances" may also be applied to this intermediate or transition state.

The range over which different solid substances may be called "ideal" (in the broader sense) varies considerably. For a number of chemically simple substances crystallizing in the regular system, this range extends up to higher temperatures than for substances of lower crystalline symmetry and with a large number of different kinds of atoms in the molecules. For a large number of crystallographically and chemically complex substances and also the amorphous substances, the transition state is possibly limited to a small region just above the absolute zero.

The distinctive feature of ideal solid substances (again in the broader sense) consists in that the *heat content U is proportional to the fourth power of the absolute temperature:*

$$U = a\,T^4, \tag{87}$$

so that *the atomic heat*[1] is given by

$$C_v = 4aT^3. \tag{88}$$

The term a varies from substance to substance. Several experimental proofs for the correctness of Eq. (88) are given in Table 5.

This important law was first developed theoretically by Debye (1912) and later established experimentally. For a number of substances the upper limit at which it is valid lies at about $C_v = 0.3$ *cal.* for many others it lies considerably lower.

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[1] In the following, the atomic heat can always be calculated for chemical compounds also. In this case it represents a mean value, which is expressed by: $\text{atomic heat} = \dfrac{\text{molecular heat}}{\text{number of atoms in the molecule}}$

TABLE 5

Cu			CaF_2			Si		
T	C_v obs	$C_v = 1.35 \cdot 10^{-5}\,T^3$	T	C_v obs	$C_v = 0.437 \cdot 10^{-5}\,T^3$	T	C_v obs	$C_v = 0.387 \cdot 10^{-5}\,T^3$
14.5	0.040	0.041	17.5	0.022	0.023	20.1	0.031	0.031
15.6	0.051	0.051	19.9	0.023	0.034	24.0	0.053	0.053
17.2	0.069	0.069	23.5	0.056	0.057	28.2	0.086	0.086
20.2	0.115	0.112	27.6	0.092	0.092	33.7	0.152	0.148
20.75	0.122	0.120	34.0	0.179	0.171	39.7	0.248	0.236
25.4	0.231	0.222	37.8	0.238	0.236	44.6	0.352	0.343
[27.7	0.32	0.287]	42.0	0.329	0.324	(53.1	0.548	0.580)

A second regularity characteristic of ideal solid substances (above the real limiting state) is that the change of volume or length l between any two temperatures is proportional to the heat content between these temperatures.

$$v_1 - v_2 \sim l_1 - l_2 \sim U_{1,2} \tag{89}$$

or, what amounts to the same thing, the coefficient of thermal expansion is proportional to the atomic heat.

$$\alpha \sim C_v \tag{89a}$$

Qualitatively, this fact has already been indicated in Fig. 15, but Table 6 is a more exact proof, as here the change of length of a diamond 3.758 *mm.* thick between 84.8 and 351.1° is compared with the heat content of the diamond. The ratio $\frac{U_{1,2}}{l_1 - l_2}$ is, indeed, very nearly constant, although the upper limit of the T^3-law has already been exceeded considerably.

TABLE 6

Temperature interval	$(l_1 - l_2) \cdot 10^4$ *cm*	$U_{1,2}$ *cal*	$\frac{U_{1,2}}{l_1 - l_2}$
84.8-194.1	0.075	31.54	420
84.8-273.2	0.247	91.4	382
84.8-296.2	0.331	126.3	382
84.8-328.0	0.471	179.0	380
84.8-351.1	0.597	222.0	372

Regarding the behavior of the remaining thermal properties of ideal solid substances, for which but little experimental material is available at present, and the general equation of state for solid substances, reference may be made to the comprehensive investigation by Gruneisen.[1]

60. The Dulong-Petit Law.—Above the range of the "ideal solid," substances assume the properties of **ordinary solids.** The most important relation common to all solid substances is that the atomic heat C_v reaches a limiting value of about 6 *cal.* at high temperatures. Table 7 indicates this.

TABLE 7

Substance	$T = 273.2°$			$T = 600°$		
	C_p	$C_p - C_v$	C_v	C_p	$C_p - C_v$	C_v
Al	5.52	0.18	5.34	6.70	0.59	6.11
Cu	5.75	0.14	5.61	6.46	0.37	6.27
Ag	6.10	0.25	5.85	6.56	0.65	5.91
Pb	6.31	0.32	5.99	7.00	0.88	6.12
Pt	6.15	0.10	6.05	6.54	0.28	6.26
KCl	6.00	0.19	5.81	6.60	0.48	6.12

A clear experimental proof of this law—which was first stated by Dulong and Petit (1818) for ordinary temperatures and C_p instead of C_v—is made difficult because in the investigation of solid substances C_p is always determined and the basis for the exact determination of the difference $C_p - C_v$ is often lacking, especially at high temperatures (see **64**). Still, the data already available show quite distinctly that neither C_p nor C_v assume exactly constant values. If the substance has a relatively low melting point, the value $C_v = 6$ *cal.* is not attained. In the other cases it is almost always appreciably exceeded, and, as a matter of fact, C_v usually shows a slight linear increase.[2] Just under the melting point a still more rapid increase is frequently observed, so that C_v, at least at this point, reaches values which are considerably above 6 *cal.* (see also Table 16).

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[1] *Ann Physik*, **4**, 39, 257 (1912)

[2] BORN, M and BRODY, E, *Z. Physik.*, **6**, 132 (1921), MAGNUS, A., *ibid.*, **7**, 141 (1921).

It is thus shown that the *law of Dulong and Petit*, even if it refers to C_v instead of C_p, *is concerned only with an approximate and not an exact regularity in the thermal properties of solids.*

61. Simple and More Complex Solid Substances.—The behavior of the atomic heat C_v at ordinary temperatures is generally not more uniform. Yet a group of substances can be selected—those which obey the T^3-law up to relatively high temperatures—for which the change of C_v with temperature can be represented by an approximately universal function; these will be designated in the following by the term **simple solid substances.** In order to demonstrate how the temperature change of the atomic heat agrees among the various simple substances, of course, the comparison cannot be made at any definite temperature, but a characteristic temperature scale must be introduced for each substance. This is done most simply by expressing the temperature of the body by the ratio $\frac{T}{\Theta}$, in which Θ is a characteristic constant for the substance and is called its **characteristic temperature.**[1] By this means of representation the atomic heat of a number of substances shows the same behavior with change of temperature (see Fig. 16, which contains a number of observations on various substances).

As a matter of principle, the atomic heat of more complex substances shows a temperature change similar to that of the simple substances given in Fig. 16, only the behavior is not uniform. Taken as a whole, the rise of atomic heat curve is in most cases not so sharp as in the normal curve. (*Example:* Hexagonal graphite and rhombic sulfur.) In such cases C_v can often be represented with some degree of accuracy by these normal functions if several Θ values are used simultaneously. As an example note the following results in sulfur, for which one-fourth of the value of C_v was calculated with $\Theta = 74$ and three-fourths with $\Theta = 510$.

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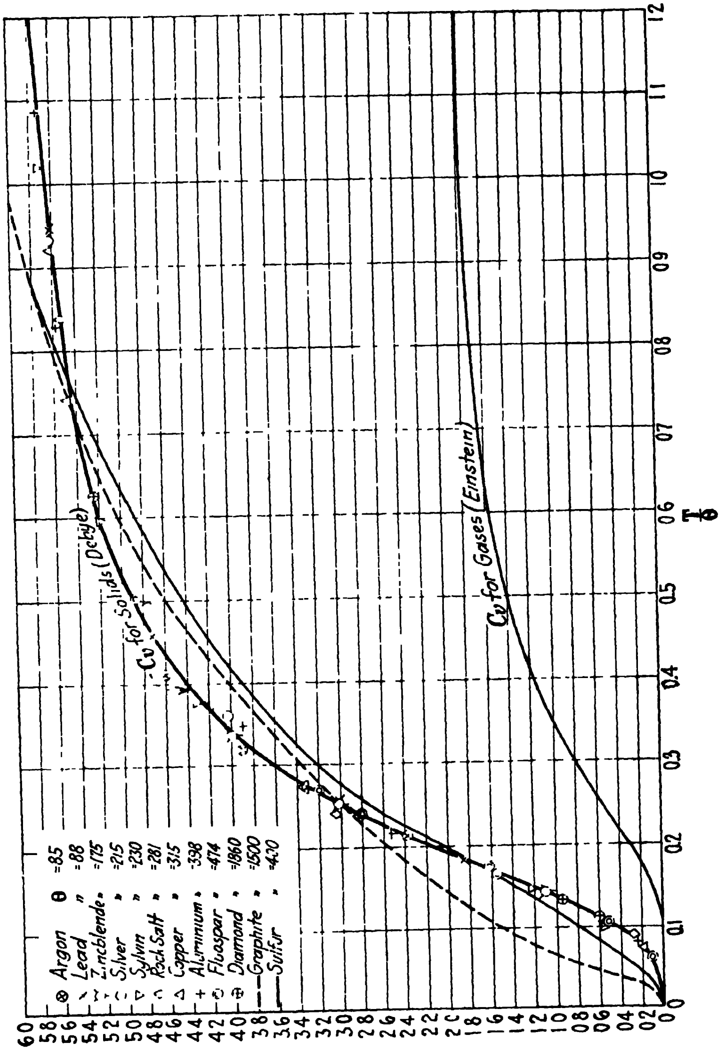
[1] * For a practical method of determining this important quantity, see LEWIS and RANDALL, *loc. cit.*, p 75, or LEWIS and GIBSON, *J. Am. Chem. Soc.*, **39**, 2554 (1917).


⊗ Argon Θ =85
Lead " =88
Zincblende " =175
Silver " =215
Sylvin " =230
Rock Salt " =281
△ Copper " =315
+ Aluminium " =398
Fluospar " =474
⊕ Diamond " =1860
Graphite " =1500
Sulfur " =430
Cv for Solids (Debye)
Cv for Gases (Einstein)
T/Θ
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
1.1
1.2
0
02
04
06
08
10
12
14
16
18
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22
24
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28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60

Fig. 16.

TABLE 8.—SULFUR

T	C'_v obs	C'_v calc
22.7	0.96	0.94
27.5	1.04	1.08
29.9	1.14	1.14
57.9	2.06	1.92
69.0	2.29	2.26
93.0	2.93	2.95
138.0	3.63	3.88
198.0	4.72	4.75
235.0	4.93	5.04
297.0	5.47	5.25

For practical and thermodynamic purposes a simple graphic reproduction of the C'_v-curve is frequently sufficient (see **223**).

62. Thermal Expansion in Non-ideal Solid Substances.—In non-ideal solid substances there is no strict proportionality between expansion of volume and heat content, yet on the whole the deviations, even up to rather high temperatures, are not so very great. For simple solid substances the coefficient of expansion increases somewhat more rapidly than C'_v; in this case the use of C'_p may be recommended, since this increases more rapidly than C'_v and therefore one may put

$$\alpha \sim C'_p \tag{89b}$$

in order to do justice to the observed results.

E. Gruneisen has indicated an important regularity which is convenient for practical purposes, but which certainly does not hold strictly; *the total percentage change of volume from the absolute zero to the melting point is approximately the same for all simple substances and amounts to about* 7.5 *per cent;* the total linear expansion between these temperatures is therefore about 2.5 per cent.

For more complexly built substances, the thermal coefficient of expansion frequently increases at a slower rate than C_v (for quartz glass, for example, it is well known to be very small over the total range; in some places it is even negative).[1]

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[1] * For a further discussion of the atomic heats of polyatomic solids, see LEWIS, W. McC., *loc. cit*, **3**, p. 76 *et seq*.

b. THERMODYNAMIC RELATIONSHIPS

63. Change of State of Ideal Solid Substances.—For the isothermal compression of a substance there is the general expression given in **28.**

$$\left(\frac{\partial U}{\partial v}\right)_T + p = T\left(\frac{\partial p}{\partial T}\right)_v.$$

According to Eq. (87), for solid substances one may put

$$U = aT^4,$$

and therefore

$$\frac{\partial U}{\partial v} = a'T^4,$$

where the differential quotient of the volume function a is designated by a'. By the transformation of Eq. (57) there is obtained first:

$$\frac{T\left(\frac{\partial p}{\partial T}\right)_v - p}{T^2} = \frac{d\left(\frac{p}{T}\right)}{dT} = \frac{1}{T^2}\frac{\partial U}{\partial v}.$$

If, now, $\frac{\partial U}{\partial v}$ is replaced by its value and integrated at constant volume between 0 and T, the result is:

$$\frac{p}{T} = \int_0^T \frac{a'T^4 dT}{T^2} + [A]$$

or

$$p = \frac{a'T^4}{3} + [A]T = \frac{a'}{3a}U + T[A] \qquad (90)$$

This equation shows that the thermal pressure p is proportional to the energy U when the substance is heated at constant volume from the absolute zero up to the temperature T, and the term $T[A]$ is neglected. That this term must vanish follows from the considerations below:

The differential quotient of Eq. (90) is

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{4a'T^3}{3} + [A] = \frac{a'}{3a}C_v + [A],$$

which, in view of Eq. (34), gives

$$\frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_p = -\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_T\left\{\frac{a'}{3a}C_v + [A]\right\} = \kappa\left\{\frac{a'}{3a}C_v + [A]\right\}.$$

The compressibility κ changes so little in the region of the ideal solid substance that it can be considered constant. Since a and a' as well as v are likewise only slightly variable, it is possible to write

$$\frac{1}{v_0}\left(\frac{\partial v}{\partial T}\right)_p = \alpha = BC_v + [A]$$

or, on substituting and integrating,

$$\frac{v - v_0}{v_0} = B'U + [A]T.$$

If this is now compared with the empirical Eq. (89) for ideal solid substances, the important result follows that for the integration constant it is necessary that

$$[A] = 0.$$

Since Eq. (57) is merely a special form of the fundamental, Eqs. (52) or (56), for the maximum work, and, further, since it is to be assumed that in ideal solid substances in the limiting state all properties, even $A_{T,v}$, become independent of the temperature, it can be expected that the integration constants occurring when the general Eqs. (52) and (56) are integrated also vanish, at least in all cases where their application is limited to solid substances. This expectation is completely confirmed by experience; it expresses the real meaning of the Nernst Heat Theorem, which will be discussed later.

64. $C_p - C_v$.—The value C_p is the one usually determined experimentally and in order to obtain C_v, which is frequently more important for theoretical purposes, the general formula, Eq. (60), is used if possible. According to **62**, $Const \times C_p^2$ can be put approximately for α^2; κ changes relatively little with the temperature. Thus,

$$C_p - C_v = A''TC_p^2 \tag{91}$$

The term A'', in which all the constant quantities are combined, varies from substance to substance and must be empirically determined for each one by determining C_p and C_v according to Eq. (60) as accurately as possible at some temperature at which α, v_0, and κ are known.

c. KINETIC THEORY

65. Atoms as the Structural Units of Solid Substances.—It has been proved that, in general, atoms and not molecules are to be considered as the smallest structural units in building up a solid substance. This follows directly from Dulong and Petit's law (see **60**), according to which it is the atomic heat which shows a distinctly regular behavior in the case of solids and not the molecular heat, as in gases.

As a more exhaustive investigation of the molecular structure of crystals shows (see **358**), the atoms in many simple substances (NaCl, KCl, diamond, metals, etc.) are actually so placed that they are linked to all their neighboring atoms in almost exactly the same way. In other cases the linkage is certainly unequal and such that certain atomic groups are more closely connected than others. But in none of these cases is it possible to speak of even an approximately rigid molecule, since each atom can be displaced along all three space coordinates from its position of rest or equilibrium; in the sense of the discussion in **32** and **52**, each atom in such molecules has three degrees of freedom. If the linkage of the atoms is unequal in different directions, as is the case with the last-mentioned substances, then, on the whole, the vibrations become very complex. On the one hand, the atomic groups (molecules) will, to a certain extent, perform vibrations about their own centers of gravity; on the other, the atoms within the vibrating group (molecule) will vibrate with respect to each other. If a less exact and therefore somewhat arbitrary treatment is sufficient, these refinements may be disregarded and only the *number of degrees of freedom, which depends only upon the number of atoms*, need be considered.

66. The Vibrations of Atoms.—Since the atoms are bound to positions of equilibrium from which they cannot depart, the only possible form of motion is vibration. For the kinetic theory of the solid state, it is, therefore, important to consider the vibrations in greater detail.

The simplest assumption which can be introduced is that all the atoms perform sine-wave oscillations, like a pendulum, of a definite frequency ν_0 so that the motion of the atoms follows according to the equation

$$x = x_0 \sin \sqrt{\frac{b}{m}} \cdot t = x_0 \sin 2\pi\nu_0 t.$$

According to **14**, this equation of motion means that the atom is drawn back to its position of rest (or equilibrium) by a force which is proportional to its distance from its position of rest (Hooke's law). It will be shown however that this assumption is permissible only as a first approximation.

Closer examination (see **68**) leads to the result that Hooke's law certainly cannot be strictly fulfilled in solid substances. Further, it can be shown that the atoms do not oscillate with a single, definite (monochromatic), characteristic frequency, but that an entire oscillation spectrum actually exists (see **76**). However, this spectrum possesses, at least in simple solids, a quite sharp intensity maximum, so that for many considerations the assumption that the atom vibrates with a definite characteristic frequency is really sufficient. The magnitude of the characteristic atomic frequencies and the methods of determining them will be referred to in **79**.

67. The Basis of Dulong and Petit's Law.—On the basis of the law of energy partition (see **31**) the mean kinetic energy of atomic vibration per gram-atom must amount to $\frac{3}{2}RT$ *cal.* However, potential energy as well as kinetic energy is involved in the vibrations. Therefore, in order to be able to give the total mean energy of the vibrating atoms, the relation of the mean potential energy to the mean kinetic energy must first be determined. It is found that on the average the potential energy is equal to the kinetic energy.

To derive this (approximately valid) law, the provisional assumption should be retained that Hooke's law holds and that the atoms perform sine-wave vibrations.

In order to remove the point[1] from its equilibrium position ($x = 0$), the force $-\mathfrak{K} = bx$ must be overcome, the potential energy of the point at the distance x, taking into consideration Eq (13), page 13, is, therefore,

$$P = \int_0^x bx\,dx = \frac{bx^2}{2} = -\frac{\mathfrak{K}}{2}x = -\frac{1}{2}mx\frac{d^2x}{dt^2}. \tag{92}$$

The kinetic energy L is

$$L = \frac{1}{2}mV^2 = \frac{1}{2}m\left(\frac{dx}{dt}\right)^2.$$

According to Eq. (8),

$$\frac{m}{2}\frac{d\left(\frac{dx}{dt}x\right)}{dt} = \frac{m}{2}\left[\frac{d^2x}{dt^2}x + \left(\frac{dx}{dt}\right)^2\right] = -P + L$$

At every point the term $\left(\frac{dx}{dt}x\right)$ has a definite value which recurs at each vibration. On the average, positive values occur as often as negative, so that in any whole number of complete vibrations they directly compensate each other. If this were not the case, the equation would state that the center of the mass must gradually shift away from its position of rest. Taking the average value of this term, indicated by a horizontal line over the symbol, over a long period of time, which can be conceived with sufficient accuracy as a large whole number times a single vibration, then the mean value of $\overline{\left(\frac{dx}{dt}x\right)}$ and also its differential coefficient $\overline{\frac{d\left(\frac{dx}{dt}x\right)}{dt}}$ vanishes and, therefore,

$$\frac{m}{2}\overline{\frac{d\left(\frac{dx}{dt}x\right)}{dt}} = -\overline{P} + \overline{L} = 0$$

---

[1]* In calculations of this nature the atoms are considered as point centers of mass.

or

$$P = L.$$

By taking the mean value for a single center of mass over a long period of time or by taking it at any point of time over a large number of vibrating centers of mass, the same result is obviously reached, since it must be assumed that the frequency with which a single center of mass occurs in a particular state (*e g*, a definite distance from the position of rest) must be the same as that of many mass centers at any point of time

Since L, the mean kinetic energy, amounts to $\frac{3}{2}RT$ (**52**), then for the total energy (kinetic + potential) per gram-atom

$$L + P = U = 2 \times \frac{3}{2}RT = 3RT$$

or

$$C_v = 3R = 5.96\ cal.,$$

as Dulong and Petit's law states, and which is in fair agreement with observations at ordinary temperatures. However, this law cannot be exactly fulfilled at high temperatures, since, as it will be shown in the following paragraphs, the force is certainly not exactly proportional to the distance from the position of rest, so that the atomic vibrations are not exactly sine curves and the mean potential energy is not quite equal to the mean kinetic energy.[1]

68. Forces of Attraction and Repulsion.—The powerful cohesion of the particles in solid substances requires the assumption of an *attractive force* between the particles; but, on the other hand, the particles approach each other only up to a certain limiting distance, for, in order further to decrease the normal distance between them, work of compression must be applied. This obviously indicates that a *repulsive force* also exists. If it is assumed that both forces are additive at every point, then without any further special assumptions it can be concluded that the repulsive force decreases more rapidly with increasing distance than the attractive force. At a definite distance between the particles, the two forces will exactly compensate each other—this corresponds to the normal volume—at smaller distances the repulsive forces overbalance the attractive forces and vice versa at distances larger than the normal. This relation is illustrated by Fig. 17, in which the dotted lines represent the behavior of the individual forces and the smooth line the resulting force. The point A, in which the latter curve intersects the abscissa, corresponds to the normal distance a of the atom at rest. The maximum of the curve at the distance a' from the zero point indicates to which point the atoms can be pulled apart by an increasing tension; if a' be exceeded, then the attractive forces again decrease or, in other words, the solid is broken. The point a' thus corresponds to the elastic limit of the body. That this limit is difficult to obtain experimentally scarcely needs to be discussed; the material is either not perfect (*i.e.*, it contains inclusions of foreign substances, holes, etc.), in which case the limit is reached too soon, or else it flows, *i.e.*, the atoms rearrange themselves during the stretching, a phenomenon exhibited even in crystals such as ice but which may be very easily observed in numerous metals[1] at temperatures far below their melting points.

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[1] M. BORN and E. BRODY (*Z. Physik*, **6**, 132 (1921)) have calculated the deviation from Dulong and Petit's law arising from this source and, in agreement with the results in **60**, found as a first approximation a correction term proportional to the absolute temperature, which brings the results to the limiting value of 5.96 *cal.*

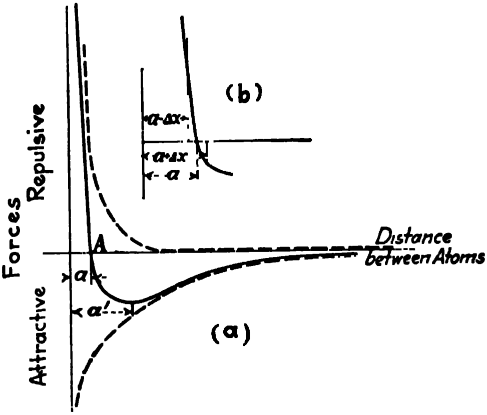

Fig 17

69. Thermal Expansion.—If the curve of the resulting force (Fig. 17*b*) is examined more closely, it will be seen that a greater force is required to cause two atoms to move a certain distance Δx towards each other than to increase the distance between them by the same amount; *i.e.*, referred to the point A, the force is unsymmetrical. As a first approximation the force may be represented by the formula

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[1]* Mark, Polanyi and Schmid, *Z. Physik*, **12**, 78 (1922)

$$\mathfrak{K} = -b\Delta x + g\Delta x^2, \tag{93}$$

which thus replaces Eq. (29).

Now if the atom vibrates about the point A, it will obviously be drawn back into its position of rest with a greater force from the point $a - \Delta x$ than from the point $a + \Delta x$; in the first case the absolute value of the force is $\mathfrak{K}_1 = b\Delta x + g\Delta x^2$; in the second it is $\mathfrak{K}_2 = b\Delta x - g\Delta x^2$, in which $\mathfrak{K}_2$ is assumed to act in the opposite direction to $\mathfrak{K}_1$ and therefore the sign of $\mathfrak{K}_2$ is reversed. As the result of this the center of vibration is somewhat displaced towards $+\Delta x$, *i.e.*, the atomic distance increases or, in other words, *the substance expands. Thus, the thermal expansion occurs as a result of atomic vibrations (heat motion) only because the law of force is unsymmetrical.*

The expansion can be prevented by applying an external force (pressure) in the direction in which the atoms are held together, this force compensating directly for the **thermal pressure** or the attempt of the substance to expand. This force, which corresponds to the thermal pressure p (at constant volume), can be brought into relation with thermal energy by means of a rough calculation,[1] if the view is accepted that the thermal pressure p must be proportional to the excess of the force $\mathfrak{K}_1$ over $\mathfrak{K}_2$ (per square centimeter) during a single vibration; *i.e.*, as a mean

$$p = \mathfrak{K}_1 - \mathfrak{K}_2 \sim b\Delta x + g\overline{\Delta x^2} - b\Delta x + g\overline{\Delta x^2} = 2g\Delta x^2,$$

if Δx or Δx^2 represent mean values for the amplitude of vibration. Now, according to Eq (92), the mean potential (thermal) energy is, at least approximately,

$$P = \frac{b}{2} \Delta x^2.$$

The kinetic energy is not exactly, but nearly, the same, so that it is possible to write

$$U = \bar{L} + \bar{P} = b\overline{\Delta x^2}$$

and thus obtain

$$p \sim U, \tag{90a}$$

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[1] P. Debye has performed an exact calculation on this problem ("Vorträge uber die kinetische Theorie der Materie und der Elektrizitat," Leipzig and Berlin (1914)).

i.e., the thermal pressure is proportional to the heat energy, which corresponds to Eq. (90) without the term $T[A]$[1] Since a thermal pressure actually develops upon heating at constant volume, it follows directly that the substance must expand at constant pressure, and, on the basis of the definition of compressibility κ,

$$p = \frac{1}{\kappa}\frac{\Delta v}{v},$$

if p is the increase of pressure calculated from the absolute zero to the temperature in question and Δv is the corresponding increase in volume. But κ as well as v vary but little at low temperatures (see **63**) and can be considered as constant. It therefore follows from Eq. (90*a*) in agreement with Eq. (90) that

$$\Delta v \sim U.$$

70. The Failure of the Classical Thermodynamics. (The Law of Energy Partition).—Even though Dulong and Petit's law ($C_v = 3R$) cannot be strictly fulfilled on account of the unsymmetrical nature of the atomic vibrations since the exact amount of the potential energy is not determined, the classical theory still demands unconditionally that the normal amount of the kinetic energy is always present, *i.e.*, in no case can the atomic heat be less than the value $\frac{3}{2}R$.

The behavior of solid substances at low temperatures (ideal solids) is certainly not in accord with this conclusion and therefore indicates even more strikingly than the molecular heat of gases that the classical theory is not able to explain the facts.

Perhaps it would not even have required these concrete, observed results in order to recognize, just as a matter of principle, that somewhere the classical theory must reach a limit in its applicability to atomic processes. Since matter is built up of atoms, the atoms themselves of smaller units, and possibly these, in turn, have a structure, a limit at which divisibility theoretically ceases does not exist. Therefore, *in the sense of the classical theory, even the individual atom and certainly tangible matter must have an infinitely large number of degrees of freedom, i.e., have an infinite heat capacity.* The fact that matter does have a finite heat capacity shows that in any case the classical theory is not valid for the very smallest structural units of matter. The behavior of the atomic heat of solid substances at low temperatures indicates that under certain circumstances the classical conceptions begin to fail even with undivided atoms.

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[1] Equation (90*a*) makes no statement regarding the presence of a term $T[A]$, since in this case even the possibility that $U \sim T$ is left open; in this event Eq. (90*a*) is in agreement with Eq (90), including the term $T[A]$, as long as the proportionality factor in Eq. (90*a*) is not fixed.

It was first attempted to retain the fundamentals of the classical conceptions and to extend them by means of additional assumptions. When, for example, the atomic heat decreased considerably at lower temperatures, this could be interpreted, according to the classical theory, to indicate a gradual loss of degrees of freedom. Such a conception appeared feasible if it was assumed that with decreasing temperature, the atoms first polymerized to form "rigid" molecules and these further to form "rigid" and increasingly large molecular complexes In the immediate neighborhood of the absolute zero (ideal solids) the whole substance must consist of a single such complex. This conception can be easily disproved, the substance must then be absolutely rigid (incompressible) at low temperatures, but this is not at all the case. Solid substances are, indeed, rather more difficultly compressible at low temperatures than at room temperatures, but they are not incompressible [1]

71. Energy at Absolute Zero.—The failure of the classical theory obviously dates from the day when heat energy was added to a system consisting of a diamond crystal at 20° *abs.* in an atmosphere of hydrogen or helium and it was found that this energy was absorbed only by the gas molecules, because the atomic heat of the diamond was practically zero.

In the investigations of this and similar facts it was first demonstrated that by cooling to a low temperature a rapidly vibrating diamond atom gave up its total vibrational energy, *i e*, at the lowest temperatures the diamond atoms persist in a state of complete rest in spite of the impacts of the gas molecules.

More recently the idea has been favored, on the basis of Bohr's model of the atom, that the atoms, are not able to lose their total vibrational energy by cooling but retain a certain amount of heat energy even at the absolute zero (**null point energy U_0**). Experimentally, no difference between the two views can be found on the basis of the measurement of the specific heats of solid substances, because by direct investigation it is only the manner in which the heat content changes and not its absolute value which is determined. (One always measures energy differences.) Perhaps the assumption that a very rapidly vibrating particle is not able to lose a part of its vibrational energy at low temperatures, due to its lack of "resonance" with its surroundings, is even more closely related to previous conceptions than the assumption that such a molecule should remain at rest in spite of all influences (bombardment by gas molecules). In the following the existence of a null point energy will be assumed, since Bohr's discovery makes it appear very probable.

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[1] * See Richards (*J. Am. Chem. Soc*, **46**, 1419 (1924)) for references to extensive researches by this author, by Bridgman and their co-workers.

72. The Hypothesis of Energy Quanta. Planck's Oscillator. The behavior of the atomic heat of solid substances and the phenomena related to it may be reproduced not only qualitatively but quantitatively by formulas which rest upon a bold hypothesis advanced by Planck in 1900. This hypothesis states that *the atoms are not able to absorb any optionally large amount of energy but only definite* **energy quanta.** The same idea may be stated in another form: *In an atom not all but only certain, quite definite, vibrational states are possible.*

Planck made his idea specific by assuming that each atom may absorb only a whole number n times a definite energy quantum ϵ_0, so that the energy of an atom is always

$$\epsilon = n\epsilon_0. \tag{94}$$

A system which follows this law is called a **Planck oscillator.** Whether individual atoms actually obey the law for Planck's oscillator exactly could be experimentally proved only with great difficulty, since in most cases, and especially in investigations of thermal properties, it is never the energy of the individual atoms but aways the mean value for a large number of atoms that is measured.

But on the other hand, since the assumption that the vibrating atoms follow this law has not yet been directly refuted by experiment, it may be retained for the present in the following considerations which are based upon Planck's oscillator.

73. Planck's Formula for the Energy Content of a System of N Oscillators.—Oscillators with only one degree of freedom (which must be doubled on account of the potential energy) may first be considered. In solid substances the oscillators, of course, possess three (doubled) degrees of freedom, but the transformation of the results obtained for a one-dimensional oscillator to a three-dimensional one involves no theoretical difficulties. As a physical example of an ordinary one-dimensional oscillator, there is the case of a diatomic gas molecule, the two atoms of which can vibrate with respect to each other along the line connecting their midpoints.

Among a large number of oscillators the heat energy is distributed similarly as among a large number of atoms, *i.e.*, unequally, for in this case also there is an energy distribution law which, of course, cannot be represented by a continuous curve since, according to Eq. (94), the oscillators can assume only certain energy values.

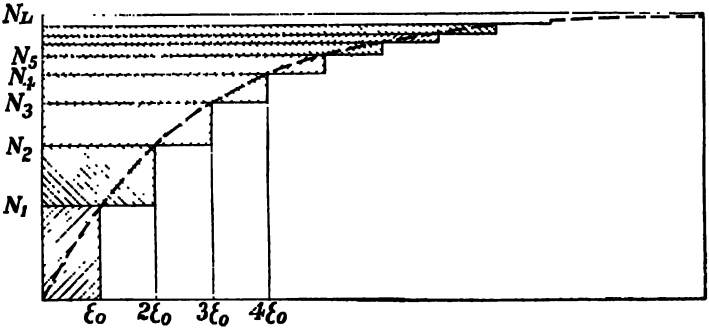

FIG. 18

If a total of **N** individual oscillators arranged in series according to their energy contents is considered, then a step-like curve, as in Fig. 18, is obtained. The smallest energy content, assuming the existence of a null point energy, amounts to ϵ_0 and it may be considered to be possessed by N_1 oscillators. The next group $(N_2 - N_1)$ has the energy $2\epsilon_0$; the third group $(N_3 - N_2)$, $3\epsilon_0$, etc. The area of the shaded step-like portions of the figure is given by

$$\epsilon_0 N_1 + 2\epsilon_0(N_2 - N_1) + 3\epsilon_0(N_3 - N_2) \quad .$$

and represents the energy content of the total **N** oscillators. It is now only necessary to find a support for the form of the step-like figure, *i.e.*, to find a definite curve (drawn as a dotted line in the figure) on which the steps rest, so that the numbers N_1, N_2, N_3, etc. can be calculated. The desired curve is, in principle, represented by Maxwell's distribution law (Eq. (69)), which for a one-dimensional oscillator has the form

$$dN = \frac{\mathbf{N}}{kT} e^{\frac{-\epsilon}{kT}} d\epsilon, \tag{95}$$

if the energy ϵ of the atoms is introduced as a variable in place of the velocity. By integrating Eq. (95), the result for the dotted curve is

$$N = \frac{\mathbf{N}}{kT}\int_0^\epsilon e^{\frac{-\epsilon}{kT}} d\epsilon = \mathbf{N}\left[-e^{\frac{-\epsilon}{kT}}\right]_0^\epsilon = \mathbf{N}\left(1 - e^{\frac{-\epsilon}{kT}}\right) \tag{96}$$

and for N_1, N_2, N_3, the corresponding values when ϵ is replaced by ϵ_0, $2\epsilon_0$, $3\epsilon_0$ . . The heat content U thus is

$$U = \mathbf{N}\epsilon_0\left\{1 + e^{-\frac{\epsilon_0}{kT}} + e^{-\frac{2\epsilon_0}{kT}} + e^{-\frac{3\epsilon_0}{kT}} + \right\}.$$

The summation of this geometric series may be performed by means of the well-known formula $s = \frac{a}{1 - q}$ and thus

$$U = \frac{\mathbf{N}\epsilon_0}{1 - e^{-\frac{\epsilon_0}{kT}}} = \mathbf{N}\epsilon_0 + \frac{\mathbf{N}\epsilon_0}{e^{\frac{\epsilon_0}{kT}} - 1} \tag{97}$$

In most cases the null point energy ($\mathbf{N}\epsilon_0$) cannot, as has already been emphasized, be directly demonstrated experimentally by means of thermal investigations, and therefore in the following will be simply disregarded.[1]

For high temperatures Eq. (97) transforms (by replacing $e^{\frac{\epsilon_0}{kT}}$ according to Eq. (25) by $1 + \frac{\epsilon_0}{kT}$, and discarding the higher terms) into

$$U = \mathbf{N}kT = RT \tag{97a}$$

in agreement with the energy distribution law. From Eq. (97) it is found that the specific heat C_v is given by

$$C_v = \left(\frac{dU}{dT}\right)_v = \frac{k\mathbf{N}\left(\frac{\epsilon_0}{kT}\right)^2 e^{\frac{\epsilon_0}{kT}}}{\left(e^{\frac{\epsilon_0}{kT}} - 1\right)^2}. \tag{98}$$

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[1] * This is logical, even in spite of the last statement of **71**, since in every experimental case dU and not U is being considered The null point energy is an additive constant term included in U and its derivative is, therefore, zero.

74. Introduction of the Characteristic Frequency ν of Oscillators.—In order to calculate the change of C_v with temperature according to Eq. (98), the magnitude of the first energy quantum ϵ_0 must be known, and, conversely, ϵ_0 can be calculated from C_v. A comparison of the specific heats found for different substances at the same (low) temperatures (see Table 5) shows immediately that the quantity ϵ_0 cannot possibly be a universal constant. On the other hand, the fact that the atomic heat curves of a large number of substances coincide if a temperature Θ characteristic of each substance is introduced and the atomic heat is represented as a function of the ratio $\frac{\Theta}{T}$, would lead to the supposition that the quantities Θ and ϵ_0 were proportional to each other, especially since Eq. (98) represents a function of the ratio $\frac{\epsilon_0}{T}$.

It can be shown that ϵ_0 as well as Θ are very closely related to the **characteristic frequency** ν of the oscillators, resulting in the simple statement

$$\epsilon_0 = h\nu. \tag{99}$$

The proportionality factor, **Planck's elementary quantum of action,**[1] is a universal constant which is extremely important for the phenomena discussed in Section D. Introducing the value of ϵ_0 from Eq. (99) into Eqs. (97) and (98) and disregarding the null point energy $\mathbf{N}\epsilon_0$, the result is

$$U = \frac{\mathbf{N}h\nu_0}{e^{\frac{h\nu_0}{kT}} - 1} = \mathbf{N} \cdot u \tag{97b}$$

$$C_v = R \cdot \frac{\left(\frac{h\nu_0}{kT}\right)^2 e^{\frac{h\nu_0}{kT}}}{\left(e^{\frac{h\nu_0}{kT}} - 1\right)^2}. \tag{98a}$$

A certain theoretical foundation for these equations, and thus also for Eq. (99), can be obtained by the proof that C_v must be a function of $\frac{\nu_0}{T}$. This may be brought about in connection with the considerations of **69** by means of a combination of kinetic and thermodynamic calculations.[1] For present purposes it will be sufficient to show that Eq. (98*a*) is completely, even if indirectly, confirmed by experience. By using the value of h obtained by the methods to be described in Section D and the various values of ν_0, likewise determined in other ways, it can be shown that Eq. (98*a*) gives the correct value for the atomic heat.

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[1] See footnote **312**.

The historical method of obtaining Eqs. (97*b*) or (98*a*) was by the law of black-body radiation. While Planck was searching for the theoretical basis underlying the empirically found radiation law (see **338**) he first obtained Eq. (97) for the energy of the electric oscillators which send out the radiation. In this case ϵ_0 must be equal to $h\nu_0$, because a general law of radiation derived thermodynamically by W. Wien (Wien's displacement law) required that the formula for the energy of oscillators should have the form $\nu F\left(\frac{\nu}{T}\right)$. Einstein then demonstrated (1907) that Eq. (97*b*) for the energy content of radiating oscillators was also valid for electrically neutral, vibrating atoms and, therefore, as a matter of principle, must represent the energy content of solid substances.

A graphic illustration of Eq. (98*a*) is given by the lower curve in Fig. 16.

75. Application of Eq. (98*a*) to the Vibrational Energy of Gases.—In the first place, Eq. (98*a*) may be tested by the increase of energy of vibration in a diatomic gas, since this represents a one-dimensional oscillator for which the theory holds true. (The vibrational energy is represented by the portion of the atomic heat which is in excess of $\frac{5}{2}R$.) For a number of gases in which the atoms carry polar electrical charges, the frequency ν_0 may be found directly by optical methods (absorption methods). The only diatomic gas for which the necessary data exist is HCl. The (mean) atomic heat on the basis of Pier's explosion investigation (see **55**) is given by the empirical formula $[C_v] = 4.90 + 0.0045t$; for ν_0 from the optically measured wave lengths ($\lambda = 3.47\mu = 3.47 \times 10^{-4}$ *cm*) the result is $0.87 \times 10^{+14}$ sec^{-1}.

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[1] The proportionality factor in Eq. (90*a*) is first determined, which gives $p = \frac{1}{\nu_0}\frac{\delta \nu_0}{\delta v}U$. (See GRUNEISEN, *Ann. Physik*, **39**, 257 (1912).) If this is differentiated with respect to T and the thermodynamic relation Eq. (67) is applied, the functional equation $\left(\frac{\delta C_v}{\delta v}\right)_T = \frac{T}{\nu_0}\frac{\delta \nu}{\delta v}\frac{\delta C_v}{\delta T}$ is finally obtained, which can be satisfied only if C_v is a function of $\frac{\nu_0}{T}$.

T	$[C_v]$ obs.	$[C_v]$ calc
1500	5.45	5.41
2000	5.68	5.66
2500	5.90	5.82

The above comparison shows that C_v may be calculated as accurately from the optically determined frequency number as it can be determined by the explosion method.

76. Internal Vibration Spectrum of Solid Substances.—In order to apply Eq. (98*a*) to solid substances, it must be multiplied by the factor 3 on account of the three degrees of atomic freedom existing in such substances. However, since it holds only for oscillators of a quite definite frequency, it cannot be applied directly to solid substances, because the atoms can by no means be considered as vibrating monochromatically; the forces acting on each atom are continually changing, due to the motion of the neighboring atoms. In an exact treatment of the problem, one cannot be limited to the consideration of a single atom. The total number of atoms performing innumerable interdependent ("coupled") vibrations must be treated together. If the vibrations were arranged according to their frequencies and it was attempted to determine their distribution among the various frequencies, an internal vibration spectrum[1] would be obtained, the character of which would, in general, differ very much from one substance to another, due to the various kinds of coupling. If, for example, the atoms are held together with different degrees of strength, then those in which the atoms were bound together very firmly (similar to the above case of a diatomic gas and also strongly marked in solid substances) would perform nearly monochromatic vibrations. In some cases this can be demonstrated. For example, Cl. Schaefer and M. Schubert[1] were able to show that a well-defined interatomic vibration in water vapor at the wave length $\lambda = 6.27\mu$ appeared only slightly different also in the solid state, ice crystals. But on the other hand, the center of gravity of atomic complexes (molecules), in so far as these are distinguishable in the solid state, also vibrate with an approximately definite frequency, so that in such cases more vibrations or, according to **77**, more values of Θ are involved in the calculation of the molecular heat than would correspond to the empirical conditions outlined in **61**.

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[1] As distinguished from the radiation spectrum

For other substances in which the atoms are nearly equally bound in all directions (in the above these have been called "simple solid substances") it might be expected that the differences between the various vibration spectra would not be very great and therefore that it might be possible to specify an **internal normal spectrum** for these substances. Debye (1912), indeed, arrived at this conclusion by means of considerations similar to those employed by Lord Rayleigh for the process of vibration in the "ether." It must be assumed that in solid substances a number of stationary waves can develop (thus the solid is first considered as a continuum); and, indeed, only such waves can form for which the wave length is a definite fraction of distance between the boundaries. The smaller the wave length (the greater the frequency number) the greater the number of waves which can develop. In this way it is found that the number of waves with frequencies between ν and $\nu + d\nu$ is

$$dZ = \frac{12\pi v_m \nu^2}{c_m^3} d\nu. \tag{100}$$

In this formula the original wave length λ is replaced by the frequency $\nu = \frac{c_m}{\lambda}$, and, besides the volume v_m, the mean velocity c_m of a sound wave passing through the solid appears. Each individual wave in the solid substance must now be treated like a degree of freedom. The total number of waves Z is, therefore, limited (if compared to a real continuum) and amounts to 3N per gram atomic weight. The spectrum represented by Eq. (100) thus cannot be expanded to any optionally large value of ν, but must cease abruptly at a definite *limiting frequency* ν_l. By integrating Eq. (100),

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[1] *Ann. Physik.* (4), **50**, 339 (1916).

$$Z_0 = 3N = \frac{12\pi v_m}{c_m^3}\int_0^{\nu_l}\nu^2 d\nu = \frac{12\pi v_m \nu_l^3}{3c_m^3}, \qquad (100a)$$

so that, Eq. (100), by substituting for c_m^3, can be written in the form

$$dZ = \frac{9N\nu^2 d\nu}{\nu_l^3}. \qquad (100b)$$

The internal normal spectrum of simple solid substances thus gives a picture such as is illustrated in Fig. 19, which shows that

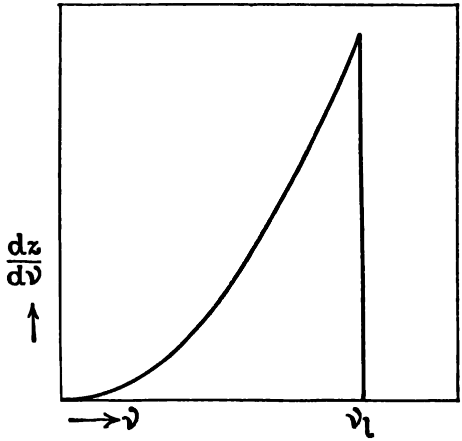

FIG 19

the vibrations near ν_l by far exceed all the other vibrations. This limiting frequency practically represents that characteristic frequency with which the majority of the atoms vibrate. However, the lack of definiteness of the frequency towards the smaller values, which is caused by the coupling, must not be entirely overlooked, because it is just this portion of the spectrum which is most influential in determining the atomic heat at low temperatures (ideal solid substances). Moreover, it must be assumed that even the more complex internal spectra, at least for the *smallest values* of ν will follow the law represented by Eq. (100).

77. The Energy Content of Simple Solid Substances.—In order to determine the energy content of a simple solid substance, the value of U in Planck's formula (Eq. (97a))[1] must be introduced for each individual vibration in the normal spectrum and then the sum (integration) taken over the entire spectrum, *i.e.*, the expression

$$U = \int_0^{\nu_l} u dZ = \frac{9N}{\nu_l^3}\int_0^{\nu_l} \frac{h\nu^3 d\nu}{e^{\frac{h\nu}{kT}} - 1},$$

is formed or, if $\frac{h\nu}{kT} = x$ is introduced as a new variable and $\frac{h\nu_l}{k} = \Theta$,

$$U = 9RT\left(\frac{T}{\Theta}\right)^3 \int_0^{\frac{\Theta}{T}} \frac{x^3 dx}{e^x - 1}. \tag{101}$$

At low temperatures $\frac{\Theta}{T}$ becomes very large; likewise x becomes very large for large values of ν, *i.e.*, those which lie in the vicinity of ν_l. It can be easily seen that for such values of x (*e.g.*, $x = 20$) the expression under the integral sign becomes very small. This means that the more rapid vibrations in the vicinity of ν_l contribute no appreciable amount to the atomic heat. Thus no error is committed if ∞ is put as the upper limit of the integral instead of $\frac{\Theta}{T}$. Then the integral assumes a constant limiting value of 6.4938 , so that

$$U = 58.45\ .\ .\ RT\left(\frac{T}{\Theta}\right)^3. \tag{101a}$$

78. The Atomic Heat of Simple Solid Substances.—The expression for C_v obtained by the differentiation of Eq. (101) is somewhat inconvenient to use; for practical purposes it is better represented graphically or in tables. A graphic reproduction of it is given by curve 1, Fig. 16, which also shows that by a proper choice of Θ it represents the experimentally observed atomic heats of numerous simple solid substances in an excellent fashion.

For low temperatures the T^3-law (59) can be obtained by the direct differentiation of Eq. (101a)

$$C_v = 464.5\ .\ \left(\frac{T}{\Theta}\right)^3. \tag{102}$$

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[1] ν_0 is replaced by ν.

The values of C_v from this equation are also in excellent agreement with the observed results. According to the very probable assumption mentioned earlier, that for the slowest vibrations the normal spectrum is actually attained by all simple solid substances, the T^3-law must, in general, also hold, at least at the lowest temperatures.

79. Methods for Determining the Characteristic Atomic Frequency.—In order to estimate the value of the theory as a whole, it is important to discover whether the values of Θ, which were necessary to reproduce the experimentally determined values of the atomic heats by means of Debye's formula (see **61**), can also be determined by other methods. Since Θ is defined by the equation $\frac{h\nu_l}{k} = \Theta$, it is possible to get direct information as to the value of the maximum frequency ν_l which can be considered as approximately the same as the characteristic frequency ν_0.

Besides the Debye equation for the specific heat (thermal method), there exist at present three other methods for determining ν_0 or Θ.

1. *Calculation from the Elastic Constants.*—According to Eq. (100*a*), ν_0 or ν_l can be calculated from the *mean velocity* c_m with which a sound wave passes through the substance $\nu_0 = c_m\sqrt[3]{\frac{3N}{4\pi v_m}}$. This can either be determined experimentally or be calculated from the following formula (which, of course, holds only for isotropic substances):

$$\frac{3}{c_m^3} = \frac{1}{c_l^3} + \frac{2}{c_t^3},$$

using the "longitudinal" and "transverse" sound velocities c_l and c_t. The latter may be calculated from the elastic constants of the substance, most simply from Lamé's constant λ, the shearing modulus μ and the density δ

$$c_l = \sqrt{\frac{\lambda + 2\mu}{\delta}};\ c_t = \sqrt{\frac{\mu}{\delta}}.$$

For crystals, the relation between the mean velocity c_m and the longitudinal and transverse velocities is less simple; moreover, a larger number of elastic constants are involved in crystals, depending upon the crystal system.[1]

If a rough approximation is sufficient and all atoms are considered as vibrating monochromatically with the limiting frequency ν_0, then it is possible to obtain ν_0 from the compressibility alone. The assumption forming the basis of this calculation is that the force involved in a rough mechanical compression or expansion is identical with that which always draws the vibrating atoms back into their position of equilibrium. In this way a relation between the compressibility κ and the proportionality factor b in Eq. (29) for an elastic force is first obtained. By applying Eq. (31) then,

$$\nu_0 \simeq \frac{3.0 \cdot 10^7}{M^{1/3}\kappa^{1/2}\delta^{1/6}}.$$

2. *Optical Methods.*—These methods are limited to a number of salts in which the atoms are electrically charged in the solid state. The atomic vibrations in such cases (at sufficiently high temperatures) become directly observable by means of the electromagnetic waves of definite wave length which they emit. The length of these waves lies between 20 and 200μ, and therefore belongs to the infra-red portion of the spectrum. Experimentally, it is more convenient to measure the absorption or reflection power at ordinary temperatures rather than the emitted rays. Near the wave lengths corresponding to the characteristic frequency of the atoms, the substance has a very high (nearly metallic) reflecting power; therefore, if a ray containing various wave lengths is reflected a number of times from surfaces of the substance to be investigated, there finally will remain in the reflected ray only those wave lengths for which the substance has an abnormally high reflecting power. These wave lengths are, therefore, called the **residual rays.**

While, of course, the measured residual rays do not give exactly the real characteristic frequency of the atoms, they at least give the approximate position much more directly.[1] Moreover, Fig. 20, which represents the reflective power of rock salt as a function of the wave length, shows definitely that towards the shorter wave lengths the drop in the curve is very much steeper than towards the longer wave lengths. This is an excellent qualitative confirmation of the behavior of the normal spectrum (Eq. (110b)).

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[1] See HOPF, A. and LECHNER, G., *Verh Deut physik Gesell*, **16**, 643 (1914); FORSTERLING, K, *Z. Physik.*, **3**, 9 (1920); and BORN and KARMÉN, *Physik. Zeit.*, **14**, 15 (1913).

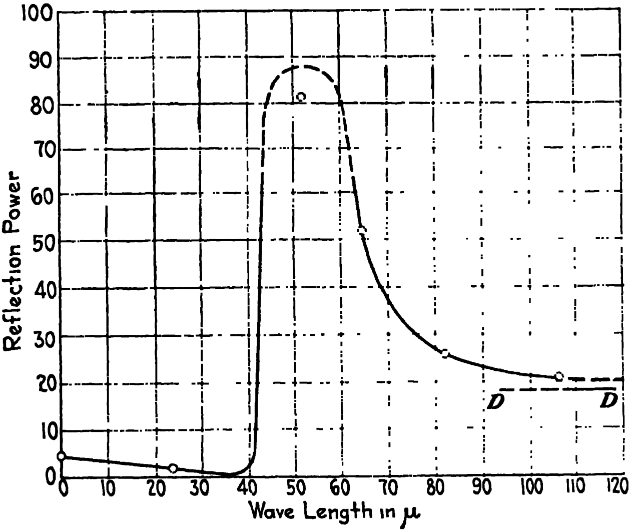

FIG. 20

3. From a simple assumption regarding the process of fusion, F. A. Lindemann developed a formula which permits the characteristic frequency to be calculated from the melting point, the atomic volume, and the molecular weight (for further details concerning this method see **134**).

80. Characteristic Atomic Frequencies.—In the following table, values of ν_l determined by the four different methods outlined above are compared for several simple substances.

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[1] A recalculation of the characteristic frequency from the wave lengths of the residual rays, which gives frequencies differing by several per cent from the older values, has been made by K. FÖRSTERLING (*Ann. Physik.*, **61**, **577** (**1920**)).

TABLE 9.—COMPARISON OF THE VALUES OF ν_l OBTAINED BY VARIOUS METHODS

Substance	$\nu_l \cdot 10^{-12}$ (*sec* $^{-1}$)			
	Thermal	Elastic constants	Optical	Melting point
Pb	1.83	1.57		1.85
Cd	3.50	3.65		2.80
KBr	3.70	..	3.70	4.50
Ag	4.50	4.60		4.40
KCl	4.80	4.73	4.80	5.65
NaCl	5.87	6.38	5.87	7.40
Cu	6.60	7.10		6.80
Al	8.30	8.65		7.70
Fe	9.45	10.1		8.30
CaF_2	9.90	10.6	9.2 13.5	11.80
Diamond	39.00			abt 33

The agreement is as satisfactory as could be expected. This indicates: (1) that the values of the characteristic frequency or limiting frequency for simple solid substances are known within about 10 per cent; (2) that the Planck-Debye theory gives correct absolute values for the atomic heat. This result is considerably better evidence as to the correctness of the theory than the circumstance that the calculated curve correctly represents the relative change of the atomic heat of simple solid substances with temperature.

81. Dependence of the Atomic Heat on Pressure.[1]—If a solid substance is compressed, the atoms are pressed closer to each other. The forces between them will, therefore, increase, and likewise the characteristic frequency ν_0 must become larger, since the increase of the force exerted upon the individual atom involves an increase in the characteristic frequency (see Eq (31) in which b is proportional to the force).

An increase of pressure (decrease of volume) *at constant temperature* therefore increases the ratio $\frac{\nu_0}{T}$, or $\frac{\Theta}{T}$, upon which the atomic heat depends. An increase of pressure thus has the same (qualitative) effect on a solid substance as a decrease of temperature, the atomic heat must decrease. This explains the statement in **58** that an infinitely great pressure transforms the solid substance into the ideal limiting state at finite temperatures. The decrease of specific heat of solids by increasing the pressure has not yet been proved experimentally, but for water a perceptible decrease has been found (5 per cent at a pressure of about 1000 *atm.*). There can be no doubt that this involves the same effect as is to be expected in solids.

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[1] See POLANYI, M., *Verh. Deut. physik Gesell*, **15**, 156 (1913).

d. APPLICATIONS

82. Theoretical Importance of Ideal Solid Substances.—The real importance of the investigations on ideal solid substances, particularly at low temperatures, lies in the fact that by this means it has been possible to learn something about a limiting state of matter for which fairly simple laws govern the phenomena. If the thermal properties of a substance, which are relatively complex at high temperatures, are examined in the neighborhood of the ideal limiting state, the relationships become sufficiently simple so that the problems which would otherwise be deprived of any exact treatment may be attacked. In this way the formulation of a third law of thermodynamics (the Nernst Heat Theorem) was finally accomplished. By means of this theorem the range of problems which can be solved by purely thermodynamic methods is considerably increased. In the Nernst Heat Theorem ideal solid substances play a similar rôle to ideal gases in the Second Law.

83. The Determination of Atomic Weights from the Law of Dulong and Petit.—The law of Dulong and Petit offers a method, although a very rough one, for determining the atomic weight A of elements or the mean atomic weight A_m of compounds. For this purpose merely the measurement of the specific heat c_p is necessary and we can then apply the approximation formula $C_p = Ac_p =$ about 6.3 *cal.* However, since this law is only a limiting law for high temperatures and since this limiting state is far from being attained by many substances, such as diamond, at room temperature, the law can be applied with certainty to the determination of the atomic weight of a new substance only if measurements of the specific heat at two different temperatures are available and show that the specific heats are not widely different over the interval concerned.

4. ACTUAL GASES

a. EMPIRICAL FOUNDATIONS

84. General Survey.—Actual gases and liquids form the transition between the two limiting states of matter, the ideal gas and the ideal solid. It might, therefore, be expected that some of the characteristics of ideal gases and solid substances would be united in them and, on account of this simultaneous appearance of different influences, that the phenomena should become more complex and the laws which govern them less simple than in the limiting states. Moreover, a division between actual gases and liquids is not absolutely necessary. Both states are closely related and under suitable conditions can even transform from one to the other continuously (see **111**). Nevertheless, the twc

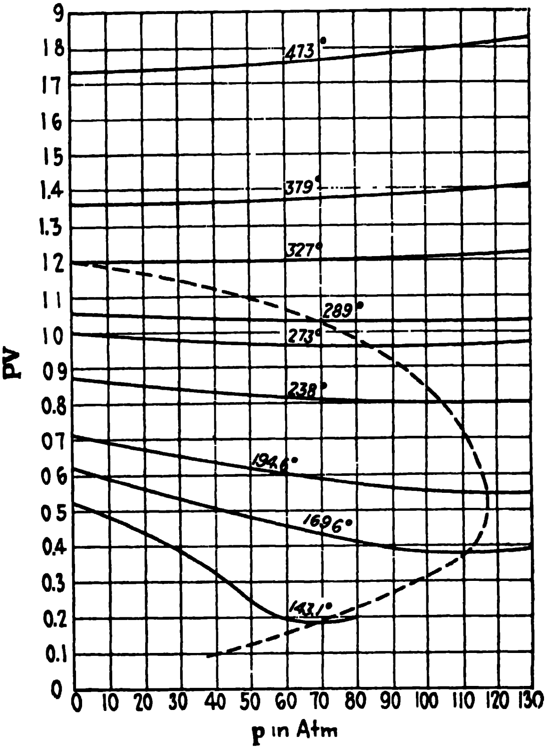

FIG. 21.

states will first be discussed separately for the sake of clearness; after that will follow a chapter devoted to transition phenomena.

85. The Behavior of the Product *pv*.—The difference between an actual gas as compared to an ideal gas is illustrated with particular clearness by the behavior of the product pv. While for an ideal gas this product remains constant as long as the temperature is constant, in actual gases it is more or less variable with pressure or volume. The variability is different at different temperatures, as is shown by the two examples in Figs. 21 and 22, which represent the pv curves for air and CO_2 at various temperatures. At low temperatures the curves show distinct minima which as the temperature increases are displaced along a parabolic path first to the right and then back again toward the left, and finally even appear to cross the point $p = 0$. It follows from this that the compressibility of an actual gas at low pres-

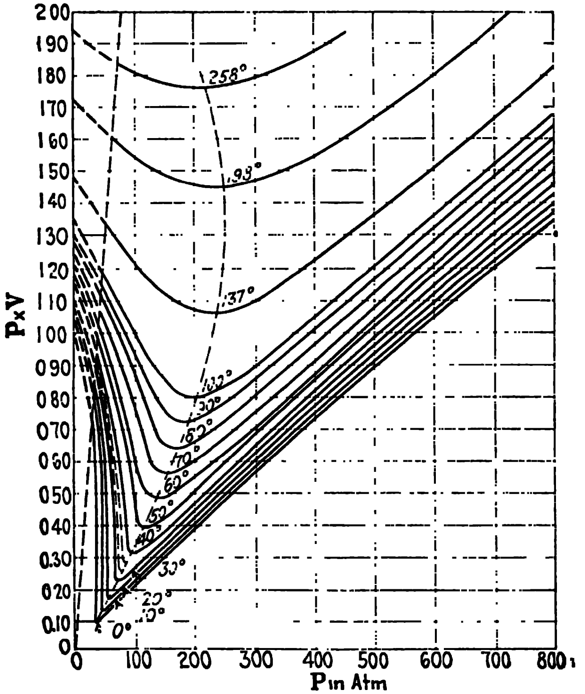

FIG. 22

sures (left of the minimum) is greater than for an ideal gas, and at higher pressures (on the other side of the minimum) it is less. It will be seen that in those curves which still possess a minimum there always exists a pressure at which the product pv has the same value as the ideal gaseous state at $p = 0$. It is further to be observed that at a definite temperature the curve becomes perpendicular to the pv-axis; therefore, at this temperature and above, the Boyle-Mariotte law $pv = Const.$ holds up to somewhat higher pressures. This temperature is thus called the **Boyle temperature** of the gas (for air it is at about 55°C.).

86. Van der Waals' Equation.—Since the pv-curve passes through a minimum, it might be immediately supposed that it would be necessary to add to the ideal gas law $pv_m = RT$ not one but two correction factors which oppose each other and at one point exactly compensate.[1] Although Clausius (1857) clearly recognized the molecular kinetic reasons for the deviation of a compressed gas from the ideal behavior, neither he nor several of his successors were able to find an equation of state which would to any degree be justified by the observations. The first to succeed was van der Waals (1873), who introduced a correction to the pressure amounting to $\frac{a}{v_m^2}$, and a volume correction of $-b$ to the ideal gas law $pv_m = RT$, so that his equation read:

$$\left(p + \frac{a}{v_m^2}\right)(v_m - b) = RT. \tag{103}$$

The quantities a and b are individual constants which must be determined empirically for each substance. (The numerical values for several gases are given in Table 19.) All gases which have the same value for b (as a matter of fact, b varies considerably less than a) show the same behavior, according to the theory of van der Waals' equation, *i.e.*, the pv-curves are similar, but definite points, such as the minima, are reached at different temperatures and pressures. This can be seen immediately; if the value of a should be doubled, then both p and T

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[1] Almost every maximum and minimum in physical functions may be explained by the simultaneous effect of two influences, the primary, simplest functions such as hold for the ideal limiting states generally proceed *without* either a maximum or a minimum

must likewise be doubled in order to give the same value for v_m. Therefore, as the value of a becomes smaller, the family of pv-curves are displaced towards the lower temperatures (compare Figs. 21 and 22); for air, with $a = 1.3 \cdot 10^6$, the temperature at which the curve becomes perpendicular to the pv-axis (the Boyle temperature) is about 55°C., while for CO_2 ($a = 3.61 \cdot 10^6$) it is between 500 and 600°C. As a result of the differences (even though small) in the values of b, the curves cannot be brought quite into coincidence with each other. In order to do this, it is necessary to introduce a special unit of volume which must be proportional to b (for further details see **113**).

As an example of what can be accomplished by Eq. (103), Table 10 should be examined. This table compares the observed and calculated values of the product pv for CO_2 at 40°C., using the values of a and b in Table 19. It will be seen that the equation reproduces the behavior of CO_2 with qualitative correctness, but quantitative deviations appear which are far beyond the limits of experimental error. Other values of a and b can, of course, be found through the use of which the agreement between observed and calculated values may be considerably improved for the lower pressures, but then the deviations at higher pressures become even greater. No matter how the values of a and b are chosen, van der Waals' equation always gives too high a value for the volume and the product pv when the pressure is high. Since at high pressures the volume correction is of very much greater importance than the pressure correction, it is accordingly necessary, at least at high pressures, to change the volume correction. In other words, b is not to be considered as a constant but as a function of the volume and perhaps also of the temperature. However, up to the present, no one has achieved another *equally simple* equation[1] which accomplishes more than the van der Waals, so that the retention of this equation is justified. Moreover, it can be shown that an equation which is to reproduce in a really exact way the behavior of a substance at all pressures, volumes, and temperatures must have at least three other constants besides the gas constant (see **115**).

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[1] The most important of the equations of state which have been advanced up to the present are summarized by J. P. KUENEN in a monograph, "Die Zustandsgleichung" (Sammlung Wissenschaft. No. 20). See also A. WOHL, *Z. physik. Chem.*, **99**, 207 (1921). * W. McC. LEWIS (*loc cit*, **1**, pp. 68 *et seq.*, and **2**, pp. 59 *et seq.*) discusses the main equations of state in some detail.

TABLE 10.—CARBON DIOXIDE AT 40°C

p	pv obs.	pv calc
1	25574	25597
5	25090	25204
10	24485	24713
25	22500	23060
50	19000	19750
80	abt. 9500	10700
100	6930	8890
200	10500	14100
500	22000	29700
1000	40000	54200

87. The Equation of State at Relatively Low Pressures.—It will be convenient at this point to test the van der Waals equation for relatively low pressures, and to observe whether it represents an approximately exact law under such conditions. For this purpose it is advantageous to change the equation into the form

$$pv_m\left(1 + \frac{a}{pv_m^2}\right)\left(1 - \frac{b}{v_m}\right) = RT.$$

Since the terms $\frac{a}{pv_m^2}$ and $\frac{b}{v_m}$ are only small corrections, $v_m = \frac{RT}{p}$ may be introduced in them and the following obtained, according to the well-known approximation formula which is applicable to small quantities:

$$pv_m = RT\left(1 - \frac{ap}{(RT)^2}\right)\left(1 + \frac{bp}{RT}\right) =$$

$$RT\left(1 - \frac{p}{RT}\left(\frac{a}{RT} - b\right)\right) \qquad (103a)$$

$$pv_m = RT(1 - Bp), \qquad (103b)$$

in which

$$\frac{1}{RT}\left(\frac{a}{RT} - b\right) = B. \qquad (104)$$

Equation (103*b*) therefore indicates only a linear variation of the product *pv* with the pressure, *i.e.*, it gives the slope of the curve at the point $p = 0$ (compare with 4).

According to Eq. (104), B may be calculated for different temperatures by using the data for a and b in Table 19. If the values thus obtained are compared with those from the observations (measurement of pv at different temperatures), by using Eq. (103*b*), qualitatively satisfactory agreement is obtained, as a rule, as Table 11 shows for hydrogen. For example, the Boyle temperature (at which $B = 0$) is located approximately correctly, at this point the pressure and volume corrections compensate directly, *i.e.*, $\frac{a}{RT} = b$. On the other hand, there are differences between the observed and the calculated values at high as well as at low temperatures, so that Eq. (104) cannot be considered as quantitatively confirmed.

TABLE 11.—VALUES OF B FOR HYDROGEN

T	$B \cdot 10^2$ obs	$B \cdot 10^2$ calc van der Waals	$B \cdot 10^2$ calc. Berthelot
16.0	+16.1	+12.22	+51.3
20.6	+ 8.2	+ 7.13	+15.8
55.5	+ 0.59	+ 0.600	+ 0.916
68.4	+ 0.28	+ 0.303	+ 0.397
90.3	+ 0.072	+ 0.087	+ 0.183
107.0	± 0	+ 0.015	[± 0]
133.2	− 0.046	− 0.0375	− 0.050
169.5	− 0.065	− 0.0649	− 0.066
273.2	− 0.058	− 0.0701	− 0.063
343.1	− 0.046	− 0.0609	[− 0.046]

After exhaustive investigations, D. Berthelot (1900) found that an equation of state, proposed in a simplified form by Clausius as early as 1881, was more serviceable than the van der Waals' equation for low pressures and high temperatures—therefore, when the gas approached the ideal state. The Clausius equation differs from the van der Waal's in that the pressure correction is $\frac{a'}{T(v_m - c)^2}$ instead of $\frac{a}{v_m^2}$ (c is a third constant); Berthelot put $c = 0$ and thus obtained:

$$\left(p + \frac{a'}{v_m^2 T}\right)(v_m - b) = RT. \tag{105}$$

If this equation is simplified for low pressures in the same way as has been done with the van der Waals', Eq. (103b) is again obtained, but B now has the value

$$B = \frac{1}{RT}\left(\frac{a'}{RT^2} - b\right) \tag{104a}$$

If the values of a' and b are determined empirically from observations at two different temperatures, it is found that for high temperatures the values of B calculated from Eq. (104a) are in somewhat better agreement with the observed values than those calculated from the van der Waals' equation. At low temperatures, however, the latter equation is apparently superior to the Clausius-Berthelot relation.

88. The Joule-Thomson Effect.—While, according to the second law of Gay-Lussac, the energy content U of an ideal gas is independent of the volume (see **42**), in actual gases it is a function of the volume, *i.e.*, when an actual gas expands without performing work (expansion into a vacuum) a change of temperature occurs. In order to measure this effect conveniently and exactly, it is expedient to apply the somewhat different arrangement used by Joule and Thomson (1853). A gas contained in a narrow, heat-insulated, wooden tube is allowed to expand from a small volume to a large one through a difficultly permeable plug. A heating or a cooling of the gas is observed (**the Joule-Thomson effect**). This, of course, is not due to the volume change of internal energy alone, but partly also to the external work ΔA performed in forcing the gas through; on the side of the plug from which the gas disappears the work p_1v_1 must be performed, while on the other side the amount $-p_2v_2$ is gained, so that the total is

$$\Delta A = p_1v_1 - p_2v_2.$$

This difference is zero only in an ideal gas.

89. Molecular Heat.—As the result of the dependence of the internal energy upon the volume, the molecular heat of actual gases is also a function of the volume (or density). In general, the molecular heat increases with increasing density, and more so at low temperatures than at high ones. Therefore, at constant density, the molecular heat of an actual gas increases as the temperature becomes lower, provided it is constant in the ideal state. At low temperatures it again decreases for high pressures, *i.e.*, it passes through a maximum. As an example of the molecular heats of an actual gas, the experimental results for hydrogen between 35 and 45° *abs.* are given in Table 12.

TABLE 12.—MOLECULAR HEAT OF HYDROGEN AT CONSTANT VOLUME

T_{abs}	Concentration (mole/liter)					
	2.67	4.89	16.95	17.20	34.5	36.2
35	3.20	3.40	abt. 4.5	abt. 4.0	3.39	3.36
37.5	3.19	3.35	3.65	3.50	3.42	3.43
40	3.18	3.28	3.43	3.39		
45	3.14	3.30	3.30	3.30		

b. THERMODYNAMIC RELATIONS

90. Isothermal Variation of Internal Energy with the Volume. The most important thermodynamic characteristic of actual gases as compared with ideal gases is that the internal energy U is a function of the volume, *i.e.*, the differential coefficient $\frac{\partial U}{\partial v}$ is not zero. From the equation of state, the relation between U and the volume may be obtained directly by means of Eq. (57)

$$\left(\frac{\partial U}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p.$$

According to the van der Waals equation,

$$\left(\frac{\partial p}{\partial T}\right)_v = \frac{R}{v - b},$$

and therefore

$$\left(\frac{\partial U}{\partial v}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_v - p = \frac{RT}{v - b} + \frac{a}{v^2} - \frac{RT}{v - b} = \frac{a}{v^2}. \quad (106)$$

Analogously, from the Clausius-Berthelot relation,

$$\left(\frac{\partial U}{\partial v}\right)_T = +\frac{2a'}{v^2T}.$$

Thus in both cases there is the same dependence on the volume:

$$\left(\frac{\partial U}{\partial v}\right)_T \sim \frac{1}{v^2}. \tag{107}$$

The latter has been tested by Amagat, who determined empirically the volume dependence of the expression $T\left(\frac{\partial p}{\partial T}\right)_v - p$, which, according to Eq. (57), is equal to $\left(\frac{\partial U}{\partial v}\right)$, and in which only experimentally measurable quantities are involved. For all the gases examined (H_2, N_2, CO_2, C_2H_4, NH_3) Eq. (107) was very accurately confirmed for small pressures and room temperature. At high pressures, however, it failed completely, due to the inaccuracy of the equation of state which was used (see Table 17).

For a finite isothermal change of energy in an expansion from volume v_1 to v_2 without the performance of work, the result from Eq. (106) is

$$U_{1,2} = \int_{v_1}^{v_2}\frac{a}{v^2}\,dv = \frac{a}{v_1} - \frac{a}{v_2}. \tag{106a}$$

91. Joule-Thomson Effect.—The Joule-Thomson effect, as has been mentioned above, is not a result of the change of internal energy alone, but is due partly to the external work performed. Indeed, since, during the investigation no heat is either added or subtracted, the change of internal energy $U_2 - U_1$ must be equal to the work performed $p_1v_1 - p_2v_2$, or, what amounts to the same thing, then

$$H_{p1} = U_1 + p_1v_1 = H_{p2} = U_2 + p_2v_2 = Const.$$

The Joule-Thomson effect is most simply characterized by the relation:

$$dH_p = \left(\frac{\partial H_p}{\partial p}\right)_T dp + \left(\frac{\partial H_p}{\partial T}\right)_p dT = 0.$$

Now, from Eq. (47a), page 56,

$$\left(\frac{\partial H_p}{\partial T}\right)_p = C_p,$$

and, further, as the result of Eq. (58),

$$\left(\frac{\partial H_p}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p.$$

For the change of temperature to be expected in the investigation, the general expression

$$dT = -\frac{T\left(\frac{\partial v}{\partial T}\right)_p - v}{C_p}\,dp \qquad (108)$$

is obtained. If the calculations are restricted to the effect at low pressures, the simplified van der Waals equation (Eq. (103*a*)) may be used. According to it

$$v = \frac{RT}{p} - \frac{a}{RT} + b,$$

therefore

$$T\left(\frac{\partial v}{\partial T}\right)_p = \frac{RT}{p} + \frac{a}{RT}$$

$$dT = \frac{\left(\frac{2a}{RT} - b\right)dp}{C'_p}. \qquad (108a)$$

As Table 13 shows, the values of dT calculated from this formula, using the values of a and b from Table 19 and with $dp = -1$ *atm.*, agree fairly well with the results actually obtained by experiment. In particular, this formula explains why hydrogen *at ordinary temperatures* shows an increase of temperature, while the other gases become cooler. The formula also indicates that for every gas there must exist a temperature $T_0 = \frac{2a}{Rb}$, at which the Joule-Thomson effect changes sign. According to van der Waals' equation, this **inversion temperature** should be exactly twice as great as the Boyle temperature T_B, since from Eq. (104) $T_B = \frac{a}{Rb}$. The Boyle temperature for hydrogen is found to be $T_B = 107°$ *abs.*, while the inversion temperature $T_0 = 222°$ *abs.*

TABLE 13.—JOULE-THOMSON EFFECT AT 15°C.

	dT calc.	dT obs.
H_2..	+0 02°	heating
O_2 .	−0 31°	−0 31°
CO_2....	−0 77°	−1 19°

92. Molecular Heat.—The simple relation (Eq. (77)) for the difference of molecular heats $C_p - C_v$ of ideal gases does not hold for actual gases. By applying the general Eq. (59), and provided the pressures are small,

$$C_p - C_v = R\left(1 + p\frac{2a}{R^2T^2}\right), \tag{109}$$

in which, on the basis of the simplified van der Waals equation (103*a*),

$$\left(\frac{\partial v}{\partial T}\right)_p = \frac{R}{p} + \frac{a}{RT^2} \quad \text{and} \quad \left(\frac{\partial v}{\partial p}\right)_T = -\frac{RT}{p^2},$$

neglecting the term $\frac{a}{RT^2}$. For the variation of molecular heat C_v with volume, $\frac{\partial C_v}{\partial v} = 0$ is obtained from the thermodynamic Eq. (61), if according to van der Waals $\left(\frac{\partial p}{\partial T}\right)_v$ is made equal to $\frac{R}{v - b}$ and therefore $\left(\frac{\partial^2 p}{\partial T^2}\right)_v = 0$. Since, as Table 12 shows, C_v actually does change, it is thus emphasized once more that the van der Waals equation does not survive a critical examination.

c. KINETIC THEORY

93. General Survey.—It has been shown in **68** that the behavior of solid substances is determined chiefly by the presence of two forces, an attractive force effective over relatively great distances, and a repulsive force effective over much shorter distances. It is highly probable that in the transition into the gaseous state these forces do not entirely disappear, since they are specific properties of the molecules or atoms and not of the state of aggregation. However, they would be involved to a smaller extent in gases because of the greater separation of the molecules. In an ideal gas, which is defined as the limiting state at infinitely low pressures, they would thus become imperceptible only because the molecules are so very far (theoretically, infinitely far) apart. As a matter of fact, the properties of actual gases can be satisfactorily explained by assuming the existence of these two forces. That is, it is possible to find a theoretical basis for an equation of state like the van der Waals, which to a certain degree corresponds with the observations, by the use of this assumption.

94. Cohesion Pressure.—Obviously, the force of attraction is first concerned in assisting the molecules to stay together. The molecules located in the interior of the substance exercise an attraction on the molecules on the surface in the neighborhood of the walls of the container. The attractive force thus acts in the same direction as pressure from the outside. In order to perform the calculation as simply as possible, van der Waals assumed that the effective range of the force of attraction of a single molecule should be great enough to include a relatively large number of the neighboring molecules. Then in the interior of a gas the forces acting on a single molecule would be completely annulled—only the molecules in a surface layer (or interface) near a partition would be drawn inwardly. The pull exerted in this way on an individual molecule at the interface is, obviously, greater as the number of molecules within its range of attraction is greater. If the range of attraction is equal to the volume v, the force becomes proportional to the density of the gas or proportional to $\frac{n}{v} = \frac{1}{v_m}$. The total attraction acting upon the molecules of the surface layer now depends upon the total number of molecules located in it, and therefore becomes greater as the number of molecules thus situated increases. Van der Waals put the number of such molecules proportional to $\frac{1}{v_m}$ which, incidentally, includes the assumption that the effect of the attraction does not of itself cause a change of density in the surface layer.

The total force π is now equal to the product of the force acting on a single molecule in the surface layer $\left(\sim \frac{1}{v_m}\right)$ and the number of molecules situated in the layer. If, for the present, this force is likewise made proportional to $\frac{1}{v_m}$, it follows that

$$\pi = \frac{a}{v_m^2},$$

in which a is a proportionality factor. If the above considerations are applied to a surface layer 1 *cm.*^{2} in area, the direct result is a force per unit area, *i.e.*, a pressure is obtained. This quantity will, therefore, be called a **cohesion pressure** which, as mentioned, acts in the same sense as the external pressure, and thus the two act additively. In place of the external pressure p in the equation of state, there now appears the sum

$$p + \pi = p + \frac{a}{v_m^2}.$$

The magnitude of the cohesion pressure in somewhat strongly compressed gases is rather considerable. For CO_2 at 40°C. and 100 *atm.* external pressure, the cohesion pressure according to van der Waals' equation is 456 *atm. i.e.*, the internal pressure in this case is 4.56 times that of the external pressure.

The calculation of the cohesion pressure, taking into account the change of density in the surface layer, involves no difficulties from the standpoint of theory, but, in order to make the calculations practicable, special assumptions are required concerning the manner in which the molecular attraction changes with the distance between the molecules. The distribution of density in the surface layer depends not only on the molecular attraction but also to a large extent on the intensity of the heat motion. At high temperatures, the latter is strong enough to stir the surface layer continuously and effectively, so that the density really becomes uniform to some degree. It will then be approximately the same as the internal density, and the van der Waals assumption therefore will be correct. On the other hand, at lower temperatures a density gradient must develop in the surface layer similar to that in the atmosphere; the lower the temperature the more easily can this density gradient develop. It will be recognized, therefore, that the distribution of the density of molecules in the surface layer, and thus the amount which this contributes to the internal pressure, must depend on the temperature and the cohesion pressure must also be a function of the temperature, even though the actual attractive force is not. This explains why an equation of state, such as Berthelot's, in which the cohesion is a function of the temperature, will to a certain degree fit the facts better than van der Waals' equation.

Von Smoluchowsky (*Ann Physik*, **48,** 1092 (1915)) has given a somewhat different derivation of the van der Waals expression for the cohesion pressure, which is in rather better agreement with the actual behavior than van der Waals'. Due to the force of cohesion, a density gradient must develop in the boundary layer which is similar to that in the earth's atmosphere (see also **152**). In the outermost layer which is in contact with the wall of the containing vessel, the number of molecules will therefore be smaller than in the interior of the gas. As the result of this, the thermal pressure at the wall is less than it would be if the density were the same as in the interior. Exact calculation shows that this reduction of the thermal pressure corresponds exactly to the effect of the cohesion pressure.

If the van der Waals assumption that the molecular attraction has a large range of influence is dropped, then, in general, the simple expression $\frac{a}{v^2}$ is no longer obtained. In particular, a would no longer be a constant but would depend on the temperature. This follows from the circumstance that, with a smaller range of influence for the molecular forces, loose agglomerations of molecules must form which cause a reduction in the number of molecules in the boundary layer, and, therefore, similar to the above, reduce the thermal pressure. However, these agglomerations decompose with increasing temperature, due to increasing molecular motion (heat motion). That the van der Waals cohesion pressure should be a function of the temperature, as it really seems to be, may, therefore, be explained as the result of a relatively small range of influence of the molecular forces, and an agglomeration of the molecules due to this, without the necessity of considering the molecular forces themselves as being variable with temperature. Equations of state, based upon the assumption that the range of influence of molecular attraction is small, were advanced by Reinganum (Dissertation Göttingen (1899), *Ann. Physik.*, **6**, 557 (1901), Tanner (Dissertation Basel (1912)); and others.

95. The Volume Correction.—While van der Waals assumed that the effective range of the attractive force was relatively great, probably greater than it really is, he limited the repulsive forces to an extremely small region in the immediate vicinity of the "surface" of the molecule, *i.e.*, he considered molecules simply as rigid elastic bodies.

By this means the problem is simplified to an extraordinary degree. As it has been shown in **48**, the thermal pressure caused by gas particles striking the walls of a vessel depends upon the number of molecules striking a unit area of the surface in 1 *sec.* At that time the gas particles were considered as mere points or, at most, very small particles, but, if these particles have finite dimensions, then the individual molecule no longer has the original volume v_m at its disposal, but a smaller one instead. In fact, as an exhaustive investigation shows,[1] the volume correction b is to be put equal to four times the characteristic volume of the molecule. Therefore, in Eq. (81) $v_m - b$ must be substituted for v_m and thus for the thermal pressure the result is

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[1] See Boltzmann, L., "Vorlesungen uber Gastheorie," **2**, p. 7. Sections I and II give an excellent and relatively easy presentation of the whole van der Waals theory. * A similar discussion will be found in Jeans, "The Dynamical Theory of Gases," p. 125, Cambridge (1921).

$\frac{Nm\overline{V^2}}{3(v_m - b)} = \frac{RT}{v_m - b}$ instead of $\frac{1}{3}\frac{Nm\overline{V^2}}{v_m} = \frac{RT}{v_m}$. Since in the state of equilibrium the thermal pressure and the sum of the external and internal pressures $p + \frac{a}{v_m^2}$ must be equal to each other, van der Waals' equation is again obtained. That this sort of treatment of the volume correction would from the very first lead one to expect nothing but approximate results and that, in fact, it leads to considerable disagreement with the observations, especially when the pressure is high, have already been emphasized. Furthermore, since solid substances are still compressible at low temperatures, it follows directly that the repulsive force extends over a finite range and is in no way limited to the "surface" of a rigid elastic sphere. The modern conceptions of the atom (see Sec. D) indicate still more clearly that molecules can be considered as being rigid only as a very rough approximation.

d. APPLICATIONS

• **96. Reduction of Actual Gases to the Ideal Gaseous State.**—With the assistance of the abbreviated Eq. (103*b*), which holds for moderate pressures, actual gases may be easily reduced to the ideal state, for[1]

$$(pv_m)_{\text{ideal}} = \frac{(pv_m)_{\text{actual}}}{1 - Bp} = (pv_m)_{\text{actual}}\,(1 + Bp).$$

If two measurements of pv at different pressures are available, B can be determined empirically for each case; otherwise, this quantity can be calculated from Eq. (104), using the data for a and b in Table 19. With the help of such a reduction to the ideal state, it is now possible to give the molecular weight determinations which are based on Avogadro's law a high degree of accuracy. By this means it was possible to determine the molecular weight of a number of elementary gases with somewhat the same accuracy as is usually attained by purely chemical methods.

97. The Joule-Thomson Effect.—The cooling of gases in the Linde apparatus for the liquefaction of gases is based upon the Joule-Thomson effect. Table 13 shows that, proceeding at ordinary temperatures, hydrogen cannot be liquefied in such a machine, because the gas becomes warmer instead of cooler. Only when hydrogen is precooled below the inversion temperature (about 220° *abs.*) does cooling accompany expansion.

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[1] * It must be remembered that Eq. (103*b*) is an approximation formula and that it is applicable only when the term Bp is small It is only under these conditions that the following can be written $\frac{1}{1 - Bp} = 1 + Bp$.

In other gas-liquefying machines, such as that of Claude, cooling is obtained by allowing the gas to perform mechanical work within the machine, which is then nullified outside by friction or similar means. However, the natural assumption that more powerful effects may be obtained by this means than by the Joule-Thomson effect is inconclusive. The practical application of this idea also involved considerable technical difficulties; in particular, it was not easy to find a lubricant suitable for such low temperatures.

5. LIQUIDS

a. Empirical Foundations

98. Differences between the Liquid and Other States of Aggregation.—The characteristic difference between a liquid and a gas is that the latter will occupy the whole of a relatively large volume and have constant density throughout, while the former will not. However, there exists no theoretical difference between a liquid and an (actual) gas. This is best shown when the substance (liquid or gas) is strongly compressed. All physical properties of the two states then become very similar. For CO_2 under a pressure of 1000 *atm.* the product pv_m is 22.415 × 1.748 *l.-atm.* at 30°C., and 22.415 × 1.780 at 40°C. And yet at 30° carbon dioxide is in the liquid state because under a sufficient pressure it does not occupy the entire volume at its disposal with uniform density, while at 40° it fills the whole vessel uniformly at any pressure, and is therefore a gas.

Compared with the solid state, there is also no theoretical, qualitative distinction. The most characteristic property of a liquid, as compared with a solid, is its relatively low viscosity, which indicates that the molecules are easily displaced. However, the particles in crystalline solid substances possess the same property, especially at temperatures just below the melting point. That this property (in solids) is finite and measurable is shown by the "flowing" of numerous metals while being worked, and the behavior of ice in glaciers.[1] The distinction emphasized by earlier writers that matter in the solid state as distinguished from the liquid state not only assumed a definite volume but also definite form, the crystalline form, likewise cannot be considered correct under all circumstances since liquid crystals or crystalline liquids are now known and their properties have been studied. A liquid which solidifies without crystallizing, usually called a "*glass*" or an *amorphous solid*, may with equal justice be classified either as a solid or as a liquid. The justification of this conception follows from the agreement between crystalline and amorphous substances with respect to many thermal properties. For example, the temperature change of the atomic heat of amorphous solids is qualitatively the same as that of crystals of low symmetry (such as triclinic crystals), while easily flowing liquids act differently.

TABLE 14 · LIQUID CARBON DIOXIDE

p	$T' = 303°$		$T' = 273°$	
	v obs.	v calc.	v obs	v calc.
75	2 92	2 92	2 04	2 20
100	2 55	2 55	2 02	2 15
150	2 30	2 30	1 97	2 06
200	2 20	2 20	1 925	2 00
300	2 07	2 07	1 86	1 93
400	1 99	2 00	1 82	1 88
600	1 88	1 89	1 75	1 80
1000	1 718	1 765	1 656	1 70

99. The Equation of State.—If the temperature and pressure range is limited to that in which liquids have a relatively low density, then the van der Waals or some related equation of state can be applied to liquids as well as actual gases. Table 14 shows that the volume (in cubic centimeters) of liquid carbon dioxide ($^{1}\!/_{22415}$ *mol.*) at 30°C. can be satisfactorily calculated by means of van der Waals' equation, but, of course, the values used for a and b must be somewhat different from those used in the gaseous state; at lower temperatures, such as 273° *abs.*, the agreement between observed and calculated values is not as good.

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[1] * For a detailed discussion of this property of solids, see BEILBY, "Aggregation and Flow of Solids," London (1921).

Tammann[1] assumed that, by applying very high pressures, liquids could be brought into an ideal limiting state, for which the laws, as for ideal solid substances and ideal gases, would be very much simplified. For pressures between 1000 and 3000 *atm.* an equation of state was actually established for a number of liquids, and was similar in appearance to the gas law:

$$(p + \pi)(v - v_\infty) = CT. \tag{110}$$

π is a *constant* cohesion pressure, v_∞ the volume at infinitely high pressures, and C an empirically determined constant. This equation states that, within the range of its applicability, the thermal coefficient of expansion (at constant pressure) as well as the tension coefficient $\left(\frac{\partial p}{\partial T}\right)_v$ is constant.

TABLE 15—VOLUME OF ETHYL ETHER ACCORDING TO EQUATION (110)

π = 2792 *atm.*, v_∞ = 0 6938, C = 3 0461

p	$T = 273\ 2°$		$T = 293\ 3°$		$T = 313\ 55°$	
	v obs	v calc	v obs.	v calc	v obs	v calc.
1	1 0000	0 9916	1 0320	1 0137	1 0680	1 0358
500	0 9465	0 9464	0 9674	0 9653	0 9889	0 9838
1000	0 9130	0 9131	0 9295	0 9293	0 9464	0 9455
1500	0 8885	0 8875	0 9020	0 9019	0 9160	0 9163
2000	0 8684	0 8673	0 8805	0 8802	0 8928	0 8931
2500	0 8522	0 8509	0 8631	0 8626	0 8740	0 8742
3000	0 8387	0 8373	0 8435	0 8430	0 8578	0 8586

At low temperatures and pressures the behavior of liquids is less uniform, so that a relatively simple and generally applicable equation of state cannot be set up. As a rule, the thermal coefficient of expansion at low temperatures is small (in some cases, such as in water just above the melting point, it is even negative) and then increases with increasing temperature. The compressibility at higher temperatures is greater than at lower temperatures, which would be expected since the volume is greater.

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[1] *Ann. Physik.*, **37**, 975 (1912); also TUMLIRZ, *Wiener Ber.*, **118** (II*a*), 230 (1909).

100. Molecular Heat.—A brief summary of the magnitude and temperature coefficient of the molecular heat of several liquids is contained in Table 16, from which the following conclusions may be drawn:

TABLE 16

Substance	State of aggregation	C_p	C_v
H_2	Solid	1 7 (14°)	
	Liquid	3 3 (14°)	
		4 40 (20°)	2 8 (20°)
			3 2 (27°)
Ar	Solid	7 8 (78 3°)	5 66 (78 3°)
	Liquid	10 50 (84 9°)	5 54 (88 4°)
		10 62 (93 9°)	5 42 (92 7°)
Hg	Solid	6 7 (233°)	5 95 (233°)
	Liquid	6 70 (273°)	5 90 (273°)
		6 59 (413°)	
		6 63 (543°)	
K	Solid	7 81 (332°)	7 26 (332°)
	Liquid	7 96 (341°)	7 25 (341°)
Na	Solid	7 49 (367°)	6 71 (367°)
	Liquid	7 43 (373°)	abt. 6 61 (373°)
Benzene	Solid	27 5 (269°)	
	Liquid	26 5 (283°)	17 1 (283°)
		33 0 (313°)	22 8 (313°)
Water	Solid	9 60 (263°)	abt. 9 0 (263°)
	Liquid	18 100 (274°)	18 090 (274°)
		18 015 (298°)	17 830 (298°)
		18 100 (330°)	17 650 (330°)

1. At ordinary and at high temperatures C_p usually increases; at low temperatures just above the melting point it sometimes shows a sharp decrease, so that in these cases it passes through a minimum.

2. In the neighborhood of the melting point C_p for the liquid is frequently appreciably larger than that of the solid; C_v generally has about the same value in both states. (Water is, obviously, an exception to this.) Therefore, if the atomic heat of a solid substance at its melting point has reached the Dulong and Petit value, then the same holds true for the liquid.

3. In case the C_v of a liquid at the melting point is rather far from the Dulong and Petit value (*e.g.*, hydrogen), it increases relatively more *slowly* with the temperature than the corresponding normal curve for a simple solid substance (see Fig. 16). For example, C_v for *Pb* increases from 2.67 to 3.69 *cal.* between 20 and 27°, while for liquid hydrogen over the same interval it increases only from 2.8 to 3.2 *cal.*

101. Surface Tension.—All liquids tend to diminish thei surface areas as much as possible and therefore (excluding other forces) assume a spherical form, since the sphere has the smallest surface for any given volume. The surface of a liquid may be compared to a stretched membrane, or, in other words, the liquid has a **surface tension** (σ). Physically, this quantity is defined as that force with which a liquid surface of 1-cm. width tends to diminish itself; it is, therefore, expressed as a force per centimeter or as a weight per centimeter. If, for example, the surface tension of water is 0.077 *g.* per centimeter, it means that a perpendicular, plane, water lamella 1 *cm.* wide is able to bear a weight of just 2 × 0.077 *g.* (in this case there are *two* surfaces, one on each side) without becoming either longer or shorter.[1]

Solid substances also have surface tension,[2] but it is seldom apparent, due to the extremely high viscosity of such substances; moreover, in the formation of crystals the *directional forces* of the molecules are very important and oppose the surface tension by tending towards the formation of plane surfaces and sharp edges.

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[1] * This gives one method by which the surface tension may be measured directly but not very accurately.

[2] One result of the surface tension of ordinary glass is the phenomenon that the zero point of a thermometer increases with the course of time, the thermometer bulb contracts of itself for the same reason as a soap bubble.

The surface tension is not a specific property of the liquid itself, but depends on the boundary substance and is, therefore, entirely different, depending on whether the liquid is bounded by a solid, a gas, or another liquid. If three media meet at one point (Fig. 23), an angle of contact is formed such that $\sigma_{1,3}$ is equal to the sum of $\sigma_{1,2}$ and the horizontal component of $\sigma_{2,3}$. If $\sigma_{1,3}$ is greater than $\sigma_{1,2} + \sigma_{2,3}$, then the liquid "wets" the solid substance, *i.e.*, the intersection point moves towards the left until the entire surface of the solid is covered with the liquid.

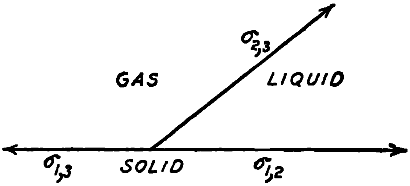

FIG 23

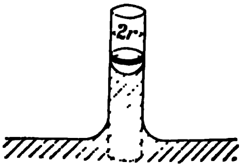

FIG 24

There are two methods for determining surface tension, besides the one mentioned in the footnote on the preceding page:

1. *The Capillary-rise Method.*—A liquid contained in a tube which it "wets" first attempts to rise in the tube against the force of gravity. But now the surface (which is to be compared to a stretched membrane) of the liquid must carry the weight of the liquid column which increases with the length of the column, and the total weight of the column really hangs on the ring-shaped contact (darkly shaded ring in Fig. 24) between glass, liquid, and gas, the length of the contact being $2\pi r$ (r = tube radius). Obviously, the liquid meniscus can rise only as far as the carrying power of the liquid surface at this ring-shaped contact will permit. The relationship therefore must be:

Carrying power = weight of the column of liquid.

The first is obviously equal to

$$\sigma \cdot 2\pi r,$$

the latter

$$\pi r^2 h\delta,$$

and, therefore,

$$\sigma = \frac{rh\delta}{2}. \tag{111}$$

This equation allows σ to be determined very conveniently from the height of ascent of the liquid in a narrow tube. The only assumption involved in the method is that the liquid really "wets" the walls of the tube.

2. **Drop-weight Method.*—This method, which was developed to a high degree of accuracy by J. L. R. Morgan[1] and others, depends upon the fact that the weight of a drop of liquid forming at the end of a narrow tube depends upon the surface tension of the liquid, provided other factors are kept constant, and thus the method is excellent for measuring relative surface tensions. For determining the absolute values, the other factors must be taken into consideration. Harkins and Brown[2] give the following derivation of the formula for this purpose: The weight W depends on the surface tension σ, the radius r of the tip from which the drop falls, and the shape of the drop. The latter is a function $f\left(\frac{r}{l}\right)$ of r and a linear dimension l of the drop, hence

$$W = 2\pi r\sigma f\left(\frac{r}{l}\right)$$

Now the cube root of the volume of the drop $v^{1/3}$ varies as a linear dimension of the drop and, therefore

$$W = 2\pi r\sigma\Psi\left(\frac{r}{v^{1/3}}\right).$$

Harkins and Brown were able to evaluate the function $\Psi\left(\frac{r}{v^{1/3}}\right)$ very accurately and thus standardize their tips. After this they could obtain absolute values for σ.

102. Eötvös-Ramsay-Shields Rule.—The only fairly general, empirical regularity which has been discovered up to the present with respect to surface tension is the rule of Eotvos (1886), modified by Ramsay and Shields (1893), according to which the dependence of the surface tension on temperature follows the simple relation

$$\sigma v_m^{2/3} = k''(T_0 - T), \tag{112}$$

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[1] **J. Am. Chem. Soc.*, **30**, 360 (1908 and later).

[2] *Ibid., **41**, 499 (1919).

where k'' is a constant which for many liquids has approximately the same value of about 2.12 (if σ is measured in *gm./cm.*). The constant T_0 is specific for each substance and, in general, is about 6° less than the critical temperature (**113**) of the liquid. Since $v_m^{1/3}$ is equal to the edge of the molecular volume v_m, if it be considered cube-shaped, $v_m^{2/3}$ must be the area of a cube surface; thus $\sigma v_m^{2/3} = \sigma_m$ the molecular surface energy or exactly that amount of work which will be performed by increasing the liquid surface by one-sixth of the surface of a gram-molecule-cube (i.e., a mole of the substance brought into the shape of a cube). If Eq. (112) is differentiated with respect to temperature, then

$$\frac{d\sigma_m}{dT} = -k'' = -2.12, \qquad (112a)$$

i.e., the temperature coefficient of the molecular surface energy is the same for numerous liquids.

However, a number of liquids do not follow this rule, but show temperature deviations and considerably smaller values of k'' than 2.12. In the main these are substances which in the liquid state apparently polymerize into double molecules or even groups of greater complexity. Since at present there is no method which is free from objection for determining the molecular weight in the liquid state, it cannot be stated with complete assurance that the failure of the Eotvos-Ramsay-Shields rule is always due to polymerization of liquid molecules. Still less is it possible to draw quantitative conclusions as to the degree of polymerization from the deviations from this rule.[1]

103. Crystalline Liquids.[2]—A number of chemically pure organic substances[3] first melt to form more or less turbid liquids; upon increasing the temperature further, the liquid suddenly becomes clear at a definite temperature. On cooling, the clear liquid again becomes turbid at the same temperature and remains so throughout the temperature range in which it is stable.

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[1] *See also J. L. R. MORGAN, *J. Am. Chem. Soc.*, **33**, 643 (1911).

[2] Among the more recent summaries concerning crystalline liquids may be mentioned that by W. VOIGT (*Physik. Zeit*, **17**, 76, 128, 152 (1916)). which, especially from the chemical standpoint, will be excellently supplemented by the monograph by D. VORLANDERS, "Kristallinische flussige Substanzen," Stuttgart (1908).

[3] Altogether about 250 substances are known which can assume the crystalline liquid state. For demonstration purposes, p-azoxyanisol and p-azoxyphenetol are especially suitable.

When observed under a polarizing microscope, the turbid liquid shows a strong double refraction similar to a crystalline aggregate of an optically uniaxial solid crystal. The discoverers of these liquids (Reinitzer, 1888; Lehmann, 1889) called them "liquid crystals," but possibly the name "crystalline liquids" proposed by Vorlander is more appropriate.

The turbid liquids can be made more or less completely clear by several methods without losing their power of double refraction.

1. They attain a certain degree of transparency if they are suspended in the form of fine droplets in an indifferent liquid.
2. The liquid becomes almost completely clear if placed between two glass plates. If clarification does not take place immediately, it can often be hastened by sliding the one plate back and forth. The optical axis of the liquid layer always places itself perpendicular to the glass plates.
3. By means of a relatively weak magnetic field, the liquid can be clarified in the direction of the magnetic lines of force (the optical axis assumes the same direction), while in the direction perpendicular to the field it still appears cloudy. At the same time, the conductivity produced by the addition of a small amount of electrolyte is increased, the increase in the direction parallel to the lines of force being particularly large.
4. By flowing (slowly) through a narrow tube, the liquid slightly clarifies itself in the direction of the tube axis, the optical axis of the liquid becoming parallel to the tube axis.

The coefficient of internal friction, or viscosity, which is the most important factor for liquids flowing *slowly* through a narrow tube (Poiseuille's law),[1] is considerably smaller in these

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[1] *Poiseuille's law simply states that the volume of liquid which passes through a capillary tube in the time t is proportional to the force F which pushes the liquid through the tube, the length l and the radius r of the tube, and the coefficient of internal friction η. The formula is

$$v = \frac{\pi F r^4 t}{8 \eta l}$$

For a given capillary tube, and keeping F and t constant, it is evident that the volume passing through it is determined entirely by the viscosity of the liquid.

substances in the crystalline liquid state than in normal (clear) liquids, even in spite of the lower temperature. These liquids, therefore, flow more readily than the corresponding normal ones. On the other hand, if the liquid is allowed to flow rapidly through the tube, the condition demanded by Poiseuille's law is destroyed and the flow becomes turbulent. The internal friction of a substance in the crystalline liquid state then becomes nearly as great as in the normal liquid.

With respect to the majority of the remaining physical properties (density, surface tension, dielectric constant, etc.), the difference between the crystalline-turbid and normal liquid states is trifling.

According to Vorlander, the ability to assume the crystalline-liquid state is limited to substances which, on the basis of investigations of their chemical constitutions, can be said to possess elongated, straight-line molecules, but, on the other hand, not every substance with an elongated molecule forms a crystalline liquid.

On increasing the temperature, some substances pass through two (some even three) crystalline liquid states, which can be distinguished by the degree of turbidity and the double refraction as well as the viscosity.

b. Thermodynamic Relations

104. Surface Tension and Surface Energy.[1]—If the surface of a liquid is increased by Δo, the work performed against the surface tension is $\sigma\Delta o$. But simultaneous with the increase of surface a thermal effect will appear which is likewise proportional to the increase of surface. As a result of the First Law, the mechanical work $\sigma\Delta o$ and the heat effect $q_0\Delta o$ involve the change of internal energy $\frac{\partial U}{\partial o}\Delta o = u_0\Delta o$ (q_0 and u_0 signify the heat effect and the energy change involved in increasing the surface by 1 $cm.^2$).

$$\sigma\Delta o + u_0\Delta o = q_0\Delta o,$$

Likewise, the Second Law in the form of Eq. (52) can be directly applied since $\sigma\Delta o$ represents a work and, therefore, in the limiting case where the process is performed reversibly, corresponds to a maximum work, hence

$$\sigma\Delta o + u_0\Delta o = T\frac{\partial\sigma}{\partial T}\Delta o. \tag{112b}$$

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[1] * For detailed discussions of this subject see the chapter by Harkins in Bogue, "Colloidal Behavior," 1, p. 142 *et seq.*, McGraw-Hill Book Company, Inc. (1924), Willows and Hatschek, "Surface Tension and Surface Energy," Blakiston's Son and Company (1923), and particularly, Freundlich, "Kapillarchemie," Leipzig (1924).

If $v_m^{2/3}$ is put in place of Δo, then, instead of $\sigma v_m^{2/3}$ and $\frac{\partial\sigma}{\partial T} v_m^{2/3}$, the values given by Eotvos' rule (Eq. (112)) can be introduced and, if v_m is considered as approximately constant, the result is

$$k''T_0 - k''T + u_0 v_m^{2/3} = k''T$$

and finally

$$u_0 v_m^{2/3} = -k''T_0 \qquad (112c)$$

Eotvos' rule may, therefore, be formulated as follows: The surface energy per mole of substance considered as being in the form of a cube is independent of the temperature and is approximately proportional to the critical temperature of the substance involved.

c. KINETIC THEORY

105. Cohesion Pressure.—The cohesion pressure which became effective even in the case of compressed gases becomes an even more prominent factor in the case of liquids. It is the real reason why the molecules of liquids hang together to a certain degree and are not able to fill an optionally large volume with uniform density as are gas molecules. The cohesion pressure is therefore to be considered as one of the characteristic properties of liquids.

As J. Meyer[1] had shown in connection with the older observations, the cohesion pressure may be directly shown experimentally in the following manner: A liquid is placed in a strong-walled glass vessel to which a spiral glass manometer is sealed. It is now warmed until the liquid fills the entire volume and all gases are carefully driven out. If the flask is now sealed off and allowed to cool, the liquid contracts, but, due to the delay in boiling (*i.e.*, the liquid is temporarily superheated), no vapor is formed at first. The manometer now shows a "negative" pressure, *i.e.*, a tension directed inwardly, which under the proper conditions may increase up to 100 *atm.* before the liquid begins to boil. Of course, a quantitative measurement of the cohesion pressure cannot be carried out by means of this simple method, since, even with the most careful manipulation, the formation of vapor always occurs long before the maximum value of the pressure is reached. In liquids, the magnitude of the cohesion pressure is reckoned in thousands of atmospheres, if, for example, the pressure π in the Tammann Eq. (110) is considered simply as cohesion pressure, it would amount to about 2800 *atm.* in the case of ethyl ether.

106. Internal Pressure.—However, it is to be observed that, besides the attractive forces which cause the cohesion pressure, there must also be a repulsive force. Only if it is assumed, as van der Waals did, that the repulsive force is limited to the immediate neighborhood of the "surface" of the molecule, can the term be ascribed merely to the effect of the attractive force. As has already been emphasized many times in the above, van der Waals' assumption is certainly not exactly correct, and it must be assumed that the range of action of the repulsive force is finite, even though smaller than that of the attractive force. It is thus expedient to combine the effects of the attractive and repulsive forces in such a way that we can speak of an **internal pressure** *which represents the difference between the cohesion pressure* π *and the repulsive pressure* π'.

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[1] "Zur Kenntnis des negativen Druckes in Flussigkeiten," Abhandlungen der deutschen Bunsengesellschaft, No. 6, Halle (1911).

The behavior of a substance is thus determined by a total of four pressures: thermal pressure (**48**), repulsive pressure, external pressure, and cohesion pressure, of which the first two tend to separate the molecules and the two latter to hold them together. In general, a definite equilibrium is produced between these pressures and the following relation results:

$$\underbrace{\textit{Thermal pressure} + \textit{repulsion pressure}}_{\textit{dispersive forces}} = \underbrace{\textit{cohesion pressure} + \textit{external pressure}}_{\textit{cohesive forces}} \qquad (113)$$

In ideal gases merely the thermal and external pressures are effective; in slightly compressed actual gases the cohesion pressure becomes barely perceptible, since in both cases the effective range of the attractive forces is relatively much greater than that of the repulsive forces. Even though the cohesion pressures of gases have appreciable values, this pressure is not sufficient to keep the gas molecules together, and, therefore, external pressure is always necessary in order to keep equilibrium with the thermal pressure, *i.e.*, the tendency of molecules to increase the volume in which they are contained by means of their heat motion.[1] By decreasing the molecular distance, the cohesion pressure increases (rather more rapidly than the thermal pressure); at distances such as exist in liquids, it is of the same order of magnitude as the thermal pressure and is, therefore able, to a certain degree, to hold the molecules together, even without the assistance of an external pressure. But since, upon further decreasing the intermolecular distance (compression of the liquid), the cohesion pressure must increase more and more, the substance would completely collapse if another opposing force, the repulsive force, did not become predominant at about this point. In the total internal pressure (cohesion pressure minus repulsive pressure) of liquids acted upon by only slight external pressure, the attractive forces by far exceed the repulsive.

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[1] Of course, gravitation sets a limit to the distance which molecules can separate. In very large masses of gases, such as the fixed stars, gravitation even becomes the determining influence. (For further information see the book by Emden, "Gaskugeln," Leipzig (1907).)

The next question is whether and how far the internal pressure may be determined by experimental means. The simplest method, while not altogether exact, yet gives results which can be used, starts with Eq. (57). The expression $\left(\frac{\partial U}{\partial v}\right)_T dv$ which represents the change of internal energy with change of volume, can be considered as related in a very simple way to the work performed by the internal energy over the volume dv, *i.e.*, the internal pressure is defined as

$$\left(\frac{\partial U}{\partial v}\right)_T = \Pi_i. \tag{114}$$

Equation (57)

$$\left(\frac{\partial U}{\partial v}\right)_T = \Pi_i = T\left(\frac{\partial p}{\partial T}\right)_v - p \tag{115}$$

may then be brought into agreement with Eq. (113); Π_i is the difference: cohesion pressure − repulsive pressure;[1] p is the external pressure. There remains only to compare the term $T\left(\frac{\partial p}{\partial T}\right)_v$ with the thermal pressure p_T. The latter is obviously defined as the pressure which a substance exercises when it is heated *at constant volume* from the absolute zero to the temperature T; therefore, the thermal pressure is

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[1] * HILDEBRAND (*J. Am Chem Soc*, **43**, 500 (1921)) defines internal pressure simply as $T\left(\frac{\partial p}{\partial T}\right)_v$ See, however, RICHARDS (*Ibid.*, **46**, 1419 (1924), especially footnote 6), who analyses the forces in a way similar to that given in Eq. (113).

$$p_T = \int_0^T \left(\frac{\partial p}{\partial T}\right)_v dT.$$

If $\left(\frac{\partial p}{\partial T}\right)_v$ is constant within the entire temperature interval, then it is actually found that $p_T = T\left(\frac{\partial p}{\partial T}\right)_v$. Now the assumption that $\left(\frac{\partial p}{\partial T}\right)_v$ is constant even at low temperatures is certainly not rigorously correct, although it agrees with Tammann's equation (Eq. (110)), but without doubt it tends (like C_v) towards the limiting value zero at very low temperatures, *i.e.*, on an average $\left(\frac{\partial p}{\partial T}\right)_v$ is smaller at low temperatures than at room temperature. Therefore, if the value for $\left(\frac{\partial p}{\partial T}\right)_v$ measured at ordinary temperatures is used, then the quantity $T\left(\frac{\partial p}{\partial T}\right)_v$ will be somewhat greater than the real thermal pressure. After all, it is probable that no great error is committed when the two quantities are simply set equal to each other, and therefore from Eq. (115) an at least approximately correct idea of the magnitude of Π, can be obtained.

Some results for the internal pressure Π, calculated from experimental data by means of Eq. (115) are given in Table 17, which includes values for two gases as well as several liquids.

TABLE 17.—INTERNAL PRESSURE Π, (IN ATMOSPHERES) AT APPROXIMATELY 20°C.

External pressure	Ethyl ether	Carbon disulfide	Ethyl alcohol	Nitrogen	Hydrogen
100	2730	....	2900	26	1.5
200	2790		2900	99	9
400	2860	3750	2900	299	16
800	2840	3670	2850	459	− 8
1500	2670	3450	2780	469	−143
2000	2530	3100	2675	383	−284
2800	2280		2400	abt 100	−578

This table shows that the value of Π_i for actual liquids is essentially constant over a wide range of pressures and it is therefore necessary to assume that within this range the attractive and repulsive forces change in about the same way with respect to the change of volume; thus, the resulting force remains constant. This conception offers nothing new, since, if the change of condition under consideration at this point is taken over a wide range of pressures, the volume, and even more so the mean distance between the molecules, changes very little. For example, the distance between ether molecules changes only about 3 per cent, while the external pressure is raised from 1000 to 3000 *atm*. At still higher pressures a decrease of Π_i is to be expected in all cases, since the repulsive pressure then becomes more effective. This decrease of Π_i is especially noticeable in the highly compressed gases N_2 and H_2. In these cases the internal pressure is first positive, then passes through a pronounced maximum, and finally (in H_2) even assumes negative values. (Thus, in this case the repulsive pressure already far exceeds the cohesion pressure.)[1]

107. Cohesion Pressure and Surface Tension.—The cohesion pressure is directly related to the surface tension because the molecules are drawn inwardly by the force of cohesion, or, in other words, the surface tends to reduce itself as much as possible. Conversely, by increasing the surface of a liquid, more molecules must be brought from the interior to the surface and thus work must be performed against the cohesion pressure.

The relation between internal pressure and surface tension results from the following consideration: It may be assumed that the molecular forces have a definite range, which means that they vanish at some finite distance, further, it may be assumed that the density of a liquid is constant up to the surface. For a molecule in the interior of the liquid, the effective (resultant) force is zero (this has already been assumed in the above), since here the forces completely counterbalance each other (Fig. 25*a*).[2] If the molecule is brought nearer to the surface (Fig. 25*b*), then only the effect of the lightly shaded area is annulled, while an attractive force corresponding to the darkly shaded area remains. The closer the molecule is brought to the surface the less are its forces counterbalanced and the greater becomes the effective force of attraction, the force begins to decrease only when the molecule gets out into the gas space. As Figs *b* and *d* show, the forces are the same for the same distance δ from the surface on *either* side. The attractive forces are thus at a maximum for a molecule at the surface and decrease symmetrically on both sides. As a result of this symmetry, the energy is also symmetrical, *i.e.*, the same amount of work must be performed in carrying the molecule of a liquid to the surface as to carry it from the surface into the gas space above. The work A' required to carry one mole from the interior to the surface is thus one-half the amount A necessary to remove it entirely out into the (dilute) gas space. Therefore (*Stefan's law*)

---

[1] * J. H Hildebrand (*J. Am Chem. Soc*, **41**, 1072 (1919)) gives a critical discussion of the various methods of determining the internal pressure, together with considerable data See also **148**.

[2] * The dot at the center represents the molecule itself. The circle is the range of its attractive forces.

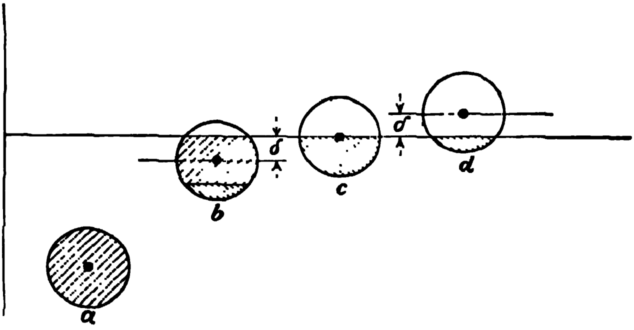

FIG. 25.

$$A' = \frac{A}{2}. \qquad (116)$$

Now if one mole at ordinary temperatures is brought from the interior to the surface or out into the gas space (evaporated), then a thermal effect will occur at the same time. In the sense of the arguments in **104**, this means that the quantity A' corresponds to an energy change u_0, it is, therefore, not to be directly considered as being the same as the work of the surface tension $\sigma\Delta o$, but it involves, in addition, latent energy to the amount of $T\frac{\partial\sigma}{\partial T}\Delta o$. For one mole it is necessary, therefore, to put

$$A' = u_0 o_N \qquad (116a)$$

In this, o_N is the surface over which one mole must be spread in order to bring all (N) the molecules to the surface. Since the mean distance between the molecules[1] is

$$\Delta = \sqrt[3]{\frac{v_m}{\mathrm{N}}}, \qquad (117)$$

---

[1] In a cube with the volume v_m there are N molecules. To each molecule there belongs a tiny cube with the volume $\frac{v_m}{\mathrm{N}}$, the edge of which corresponds to the mean distance between the molecules.

then

$$o_M = \frac{v_m}{\Delta} = \frac{v_m}{\sqrt[3]{\frac{v_m}{N}}} = v_m^{2/3}\sqrt[3]{N} \qquad (118)$$

The amount of energy which is required to bring one mole from the interior of the liquid into the gas space, i e, to evaporate it, and which corresponds to A in Eq. (116), is nothing but the internal molecular heat of evaporation Λ_i (123). Therefore, from Eqs (116), (117), and (118) the following relation must be satisfied:

$$\Lambda_i = 2u_0\, v_m^{2/3}N^{1/3} \qquad (119)$$

In columns 3 and 4 of Table 18, experimental values of Λ_i for several substances are compared with $2u_0v_m^{2/3}N^{1/3}$, the term u_0 being determined according to Eq (112b) from the surface tension and its temperature coefficient

TABLE 18

Substance	$\frac{a}{v_1} - \frac{a}{v_2}$	Λ_i obs.	$2u_0v_m^{2/3}N^{1/3}$
Hg	?	14000	15400
C_6H_6 . .	4800	6600	4800
Aniline. ...	7000	9100	5900
O_2..	1330	1680	1120

The table indicates that the relation expressed in Eq. (119) is fairly good in some cases, such as Hg, and in others at least gives the correct order of magnitude for Λ_i. Possibly, the main reason for the deviations is that the density in the surface layer is not constant, as it was assumed to be. It is clear that this effect would be more pronounced in the easily compressible liquids than in difficultly compressible ones, such as mercury

The energy required to transfer one mole of a substance from the liquid to the gaseous state must, obviously, be equal to the difference in the internal energy possessed by the substance contained in volume v_2 (gas) and the volume v_1 (liquid). Therefore, according to Eq. (114), the relation must be

$$U_{1,2} = \int_{v_1}^{v_2} \Pi_i\, dv = 2u_0v_m^{2/3}N^{1/3}. \qquad (120)$$

This equation is, of course, only approximately true, but it represents the general relation between the cohesion pressure and the surface energy or surface tension

The integral in Eq (120) can be evaluated if the relation between cohesion pressure and volume is known If the van der Waals' equation is applied, the result from (106a) is

$$\Lambda_i = \frac{a}{v_1} - \frac{a}{v_2} = 2u_0v_m^{2/3}N^{1/3}. \qquad (120a)$$

This equation can give only the order of magnitude of the actual value, since van der Waals' equation is certainly not correct for liquids at low temperatures, but it proves to give rather better results (compare columns 2 and 3, Table 18) than might be expected. The agreement between the second and fourth columns is still better, but this is obviously so because in the calculation of $\frac{a}{v_1} - \frac{a}{v_2}$ and $2u_0v_m{}^{2/3}\mathrm{N}^{1/3}$ the same factors were neglected each time.

108. The Heat Motion of Molecules in the Liquid State.—On the basis of **100**, the following statements with regard to the mode of molecular motion in the liquid state may be made:

Although the molecules are movable and not bound in fixed positions, the fact that the atomic heat at high temperatures is approximately 6 *cal.* indicates that the molecular vibration in a liquid is similar to that in solid substances. Accordingly, it must be imagined that the liquid molecules describe irregular zigzag paths in which the angles at the points of reversal of path are very pointed, so that two complete vibrations following immediately upon each other pass over practically the same path, and that within a sufficiently short time interval the motion is not to be distinguished from an ordinary vibration. This sort of vibrating motion is called *quasiperiodic,* and its properties, disregarding the gradual shift of the center of vibration, are the same as those of ordinary vibration (pure periodic motion).

Even though the constant in the Dulong and Petit law for C_v appears upon closer examination to be somewhat smaller in the case of liquids than solids, yet with regard to heat motion, monoatomic liquids in all cases are more similar to solid substances than to monoatomic gases with an atomic heat $C_v = 3$ *cal.* This point indicates quite clearly that van der Waals' equation is not applicable to liquids, because, according to **92**, C_v for liquids must be the same as for gases.

The increase of the atomic heat of liquids with temperature is slower than that of solids. In the light of quantum theory, the explanation of this may possibly be that in liquids the quantity Θ or the frequency ν_i (**77** *et seq.*) increases relatively fast with increasing temperature. Since the atomic heat depends on the ratio $\frac{T}{\Theta}$, the effect of an increase of T, when accompanied by an increase of Θ, must in all cases be lessened. Moreover, up to the present neither Θ nor ν_i has been determined with any certainty for liquids, as it has been for solids, so that an exact test of the existing relationships is still lacking.

Whatever the decrease of atomic heat (with increasing temperature) just above the melting point may mean, it obviously involves the same sort of phenomenon as in actual gases for which the atomic heat, according to Table 12, likewise decreases with increasing temperature. · The negative temperature coefficient in these cases is most probably due to a sort of "flocking together," that is, a sort of irregular agglomeration of molecules, which in liquids would probably even be able to take on the character of a polymerization or association. These agglomerations would be destroyed by increasing the temperature, but their destruction requires a certain expenditure of energy, so that at low temperatures, as long as the agglomerations are present, the heat content and the atomic heat are greater than normal

109. Crystalline Liquids.—Since it has been customary to consider the molecular state in normal liquids to be completely disordered like that of gases, it was somewhat difficult at first to understand the properties of crystalline liquids (**103**). At present, it may be said with assurance that the molecules in a crystalline liquid are not completely disordered.[1] However, in comparison with real crystals, the orderly arrangement appears to take place only in one direction. It must thus be supposed that the elongated molecules which are typical of crystalline liquids place themselves with respect to each other in much the same way as sticks in a bundle, whereby they are, of course, not grown together (as in real crystals) but may be very easily shifted in the direction of their long axis. Indeed, in a bundle of sticks it is much easier to remove one stick in the direction of its long axis than perpendicular to it. In a large volume of liquid under no special external forces, a large number of liquid crystal bundles of microscopic dimensions are formed. The irregular positions of these with respect to each other cause the cloudiness in the liquid. By relatively weak influences (magnetic field, attraction of the walls of the vessel, etc.) it is possible to orientate the bundles so that their axes are parallel and the liquid becomes transparent at least in the direction of the axis.

The other characteristic properties of crystalline liquids mentioned in **103** may also be explained, at least qualitatively and without involving too great a stretch of the imagination, on the assumption that bundles of molecules are present in such liquids. Concerning the internal friction, it may be easily seen that, when these liquids flow slowly through a tube, the bundles have the opportunity of orienting themselves so that their long axis is parallel to the tube axis. This is the position in which least resistance is offered to the motion of the bundles. If the flow is rapid, so that the motion becomes turbulent, the bundles are whirled about so strongly that they are not able to orient themselves in the direction of the tube axis and, therefore, the frictional resistance becomes as in transparent, molecularly disordered liquids [1]

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[1] This statement is essentially that given by Bose (1909) in the theory of the formation of groups or "swarms" in crystalline liquids

Strange to say, there obviously exist different kinds of molecule bundles in many cases, as the occurrence of several crystalline states shows.

6. THE TRANSITION OF CHEMICALLY HOMOGENEOUS SUBSTANCES FROM ONE STATE OF AGGREGATION INTO ANOTHER

a. Empirical Foundations

110. State of Aggregation and "Phase."—A state of aggregation which is stable within a definite range of temperature and pressure will be called a **phase.** Each substance has only one gas phase; as a rule, only one liquid phase (in crystalline liquids several); and in most cases several crystalline solid phases. On the other hand, the amorphous state does not represent a distinct phase in this sense.

111. Vapor Pressure.—The transition from one phase to another takes place under certain conditions of temperature and pressure which will be considered in greater detail in the following.

As long as a single substance exists in only one of the three states, gaseous, liquid, or solid, it occupies a definite volume at a given temperature and pressure. If the temperature changes, and the pressure is kept constant, then another volume is obtained, *i.e.*, the volume is a single valued function of pressure and temperature

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[1] F. Kruger has shown that the behavior of crystalline liquids with respect to their internal friction is also in agreement with other theories besides that of the formation of bundles.

If, however, the total volume of a substance which is partly gaseous and partly liquid (or solid) is changed, the pressure remains constant as long as both states are present. This pressure which is constant for any given temperature and under which liquefaction (by decreasing the volume) or evaporation (by increasing the volume) takes place is called the **vapor pressure.** When the volume is decreased to the point where no more gas is present, the pressure begins to increase upon further reduction of volume, but increases very much more rapidly than in gases.

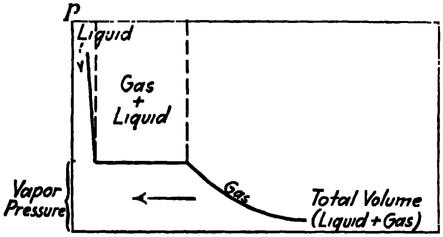

FIG. 26

The volume-pressure diagram (**isotherm** = at constant pressure) of a substance in the range of liquefaction is given in Fig. 26.

112. The Coexistence of Liquid and Vapor According to van der Waals' Equation.—As mentioned in **99,** van der Waals' equation may be applied not only to the gaseous state but also to liquids, particularly at higher temperatures, although different constants must be used in the two cases in order to represent the experimental results accurately. Therefore, this equation may be examined at once as to its ability to represent the transition gas-liquid.

A van der Waals' curve for CO_2 at 13.1°C., extending from the gaseous state (low pressures) to the liquid state (high pressures), is illustrated in Fig. 27. The equation gives an S-shaped curve in place of the observed horizontal straight line *FG* which corresponds to the vapor pressure and which joins the two branches of the curve, *BTG* representing the gas and *FA* the liquid. The branches *GN* and *FM* have occasionally been attained experimentally, although they represent labile or metastable states corresponding to a supersaturated vapor or a superheated liquid. The portion *NCM* is not physically attainable, since it involves a substance with a negative compressibility (the volume decreases with decreasing pressure). Such a substance has not yet been observed. If it is now supposed that a substance under slight pressure (large volume) could be compressed by gradually increasing the pressure until the point *N* is reached, then the volume would suddenly jump (the pressure remaining constant) to a point above *F* and again continue its change from this point. The portion *MN* cannot be passed over from the low-volume side either; in the extreme case the point *M* could be reached, but from here (if the pressure is kept constant) the volume jumps to a point to the right of *G*.

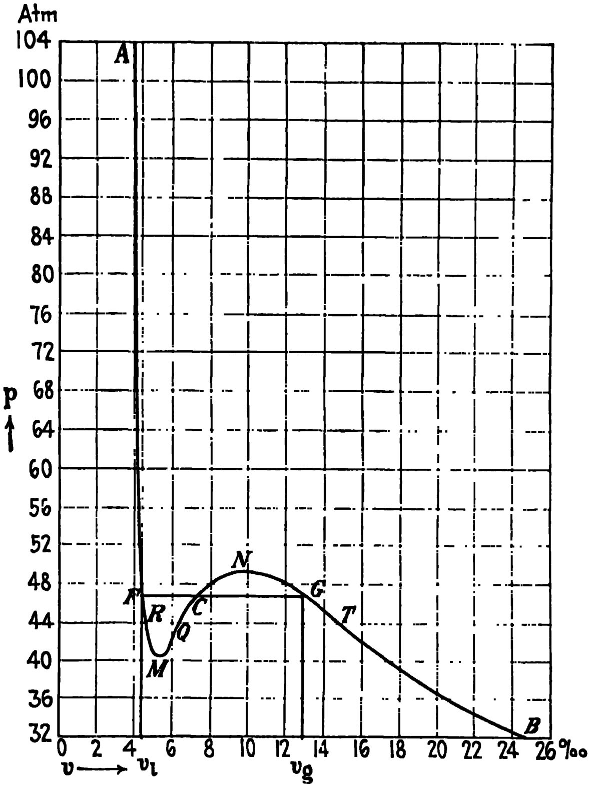

Fig. 27.

Thus, in the region of the transition, gas-liquid, van der Waals' equation represents a labile state, of which only a part is experimentally attainable and the liquefaction or evaporation at constant pressure is not accounted for. With the assistance of a thermodynamic consideration this gap may be filled:

If it be required, on the basis of the Second Law, that the work of expansion during the actual evaporation at constant pressure must be just as great as the labile van der Waals transformation along the S-shaped portion of the curve, the area of the surface *FMC* must be equal to that of *CNG* (Fig. 27). By this means the position of the horizontal vapor-pressure line within the van der Waals curve is fixed.[1]

113. Critical Phenomena According to van der Waals' Equation. Considered algebraically, the van der Waals equation is an equation of the third degree with respect to v_m and may be written in the form

$$v_m^3 - \left(b + \frac{RT}{p}\right)v_m^2 + \frac{a}{p}v_m - \frac{ab}{p} = 0. \qquad (103c)$$

Therefore, at a given temperature and pressure there are three roots of the equation, *i.e.*, three values for v_m. If the factor $\left(b + \frac{RT}{p}\right)$ is sufficiently small (therefore, at low temperatures), all three roots are real. According to the reasoning in **112,** one of these roots corresponds to the gas, the second to the labile S-shaped portion of the curve, and the third to the liquid. If the temperature is gradually increased, the S-shaped portion and the vapor-pressure line become smaller and smaller until finally a temperature is reached at which they no longer exist. A number of van der Waals' curves are illustrated in Fig. 28. The values of a and b for carbon dioxide given in Table 19 were used in making the calculations. With the exception of the labile portions, the curves are qualitatively in good agreement with experiment.

That point in which the three roots of v_m coincide is called the **critical point,** and therefore we speak of a **critical volume** φ_0, at **critical pressure** π_0 and a **critical temperature** ϑ_0. Above

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[1] * This was first pointed out by Maxwell. The details of the reasoning by which this conclusion is reached are given by W. McC. Lewis, *loc. cit.*, **2,** p. 72.

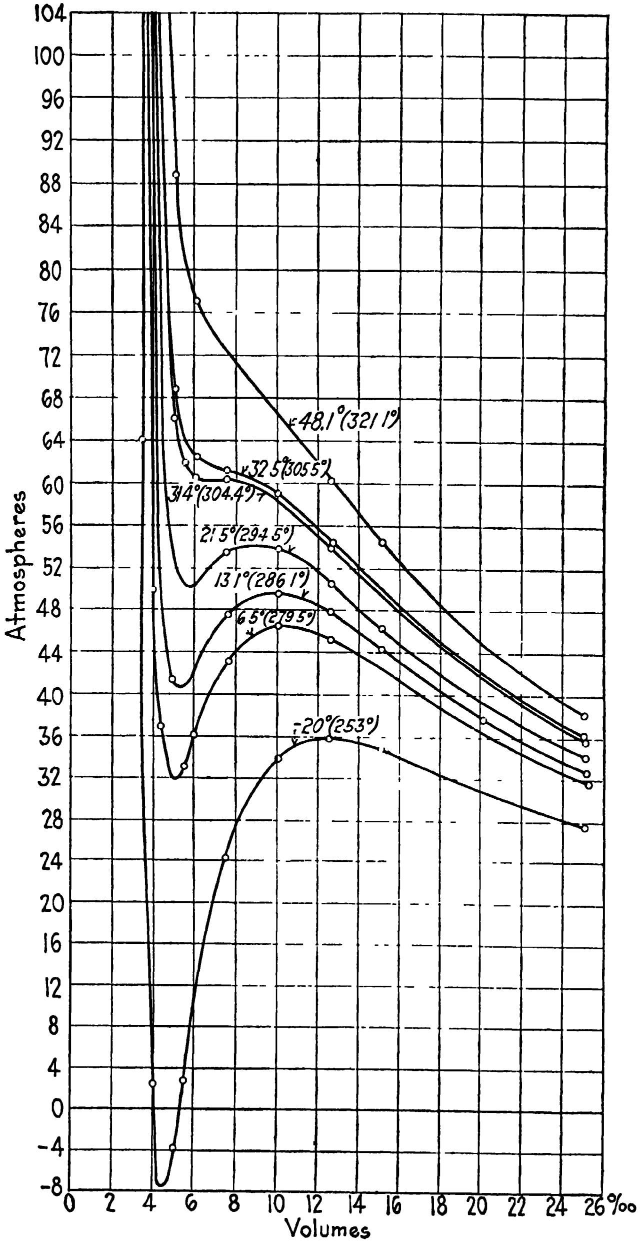
104
100
96
92
88
84
80
76
72
68
64
60
56
52
48
44
40
36
32
28
24
20
16
12
8
4
0
-4
-8
Atmospheres
+48.1°(321.1°)
+32.5°(305.5°)
31.4°(304.4°)
21.5°(294.5°)
13.1°(286.1°)
6.5°(279.5°)
-20°(253°)
0
2
4
6
8
10
12
14
16
18
20
22
24
26‰
Volumes

FIG. 28.

the critical point only one root is real; the others are imaginary and, therefore, without physical significance. Above the critical point the liquid cannot exist and the substance is thus in a region in which only the gaseous state is possible. The curve at 31.4° (the **critical isotherm**) can be considered as the boundary between the regions where liquids and gases exist.

However, it would be erroneous to speak of a really sharp boundary between the gas and liquid states. It has already been emphasized that a compressed gas has almost exactly the same properties as a (compressed) liquid. The only difference between the two is that by releasing the pressure sufficiently the liquid evaporates, *i.e.*, changes its state, while the gas remains in its original state of aggregation.

There is thus the possibility of changing a liquid into a gas by a *continuous* process, without really evaporating it. This may be done by first compressing it to a pressure which is greater than the critical pressure, heating it above the critical temperature, then expanding and allowing it to cool. In this way the passage through the zone of condensation *FG* (Fig. 27) is avoided.

114. Calculation of *a* and *b* from the Critical Data.—The position of the critical point may be calculated without difficulty from the constants *a*, *b*, and *R*. Since at the critical point the three roots of v_m must coincide and be equal to φ_0, the critical volume, the following equation results:

$$(v_m - \varphi_0)^3 = v_m^3 - 3\varphi_0 v_m^2 + 3\varphi_0^2 v_m - \varphi_0^3 = 0.$$

By applying Eq. (103*c*) (p. 164) at the critical point and, therefore, substituting π_0 for *p*, and ϑ for *T*, the result is

$$v_m^3 - \left(b + \frac{R\vartheta_0}{\pi_0}\right)v_m^2 + \frac{a}{\pi_0}v_m - \frac{ab}{\pi_0} = 0.$$

Equating the coefficients of equal powers of v_m, we get

$$\varphi_0^3 = \frac{ab}{\pi_0}$$

$$3\varphi_0^2 = \frac{a}{\pi_0}$$

$$3\varphi_0 = \left(b + \frac{R\vartheta_0}{\pi_0}\right).$$

From these it follows that

$$\varphi_0 = 3b; \quad \pi_0 = \frac{a}{27b^2}; \quad \vartheta_0 = \frac{8}{27}\frac{a}{bR}, \tag{121}$$

or, if R, a, and b are to be calculated from the critical constants,

$$\left.\begin{aligned} R &= \frac{8}{3}\frac{\pi_0\varphi_0}{\vartheta_0} \\ a &= 3\pi_0\varphi_0^2 = \frac{27R^2\vartheta_0^2}{64\pi_0} \\ b &= \frac{\varphi_0}{3} = \frac{R\,\vartheta_0}{8\,\pi_0} \end{aligned}\right\}. \tag{122}$$

Since the critical data may be quite accurately determined experimentally by investigating the critical isotherm, Eq. (122) offers a convenient way of determining a and b. However, since φ_0 can generally be measured with considerably less accuracy than π_0 and ϑ_0, it is best to use those relations in which φ_0 does not appear for calculating a and b. Some numerical values are given in Table 19, which are intended to be used in Eq. (103) when this refers to one mole, the pressure being expressed in atmospheres and the volume in cubic centimeters.[1] If the values are to be applied to n moles, then a must be multiplied by n^2 and b by n. Thus, starting with a gas volume of 1 *cc.* at 0°C. and 1 *atm.* pressure, so that $n = \frac{1}{22415}$ mole, then a must be multiplied by $1.99 \cdot 10^{-9}$ and b by $4.46 \cdot 10^{-5}$.

TABLE 19.—THE VALUES OF a AND b IN VAN DER WAALS' EQUATION

Formula	Substance	ϑ_0	π_0	b in *cc.*	a in *cc.*^{2} × *atm*
CH_3COCH_3...	Acetone	505.8	52.2	99.4	$13.92\ 10^6$
Ar	Argon...... .	155.6	52.9	30.2	$1.303\ 10^6$
Cl_2	Chlorine	419.0	93.5	46.0	$5.34 \cdot 10^6$
C_6H_5F.	Fluorbenzene	559.6	44.62	128.5	$19.98\ 10^6$
He	Helium	5.16	2.26	23.42	$0.03253\ 10^6$
CO_2..........	Carbon dioxide	304.1	73.00	42.75	$3.609 \cdot 10^6$
O_2.............	Oxygen.	154.2	50.8	31.18	$1.332 \cdot 10^6$
N_2.............	Nitrogen .	126.0	33.5	39.6	$1.345 \cdot 10^6$
H_2O.	Water	647	217.5	30.55	$5.47 \cdot 10^6$
H_2.. ..	Hydrogen	33.18	12.80	26.70	$0.244 \cdot 10^6$

---

[1] * Note that, since the term $\frac{a}{v_m^2}$ is subtracted from p, it must have the dimensions of a pressure. Hence a must have the dimensions pressure × (volume)^2.

115. The Reduced Equation of State.—If the values from Eq. (122) are substituted in the original van der Waals equation, we first obtain

$$\left(\frac{p}{\pi_0} + \frac{3\varphi_0^2}{v_m^2}\right)\left(3\frac{v_m}{\varphi_0} - 1\right) = 8\frac{T}{\vartheta_0},$$

or if the relations

$$\pi = \frac{p}{\pi_0}, \quad \varphi = \frac{v_m}{\varphi_0}, \quad \vartheta = \frac{T}{\vartheta_0},$$

are introduced, we get

$$\left(\pi + \frac{3}{\varphi^2}\right)(3\varphi - 1) = 8\vartheta. \tag{123}$$

The quantities, π, φ, and ϑ are called the **reduced pressure, reduced volume,** and **reduced temperature.**

The significance of Eq. (123) may be expressed as follows: By introducing the reduced quantities, all constants specific for individual substances vanish from the equation of state, and as an equation of state a *universal function* is obtained which claims to be valid for all substances. For given values of π and ϑ all substances have the same values of φ. If two substances are considered at such pressures and temperatures that their values of π and ϑ are the same, then these substances are said to be in **corresponding states.** The general considerations required to bring the equation of state into the form of a universal function are grouped together in the **theorem of corresponding states.** This is independent of the special form of the van der Waals equation. It merely states that in the equation of state of a substance only three constants are necessary. These constants can, as in the above, be replaced by the critical data in such a way that only the **reduced quantities** are present.

A general proof of the theorem of corresponding states can be performed in various ways independently of a special equation of state. A convenient graphic method consists in observing whether the pv-curves of different substances can be made to coincide by suitably changing the measuring unit used in plotting. (This corresponds to the variation of reduced quantities.) The total result of a large number of tests of the theorem is essentially a negative one. It is approximately confirmed only for chemically related substances with critical temperatures which are not very different. As soon as substances which do not satisfy these two conditions are compared, the theorem fails. It thus seems as if an equation of state which really agrees with the facts would require at least one more constant than the van der Waals equation, that is, a total of four constants.[1]

116. Vapor Pressure and Temperature.—The vapor pressure of a liquid usually increases rapidly with the temperature, and as a first approximation the logarithm of the vapor pressure is a linear function of the reciprocal temperature $\left(\frac{1}{T_{abs}}\right)$, *i.e.*, if the logarithm of the pressure is plotted as a function of $\left(\frac{1}{T_{abs}}\right)$, an approximately straight line is obtained. In the exact vapor-pressure formula, which is based on the Second Law, this logarithmic relation plays an important part (compare **128**). At relatively high temperatures, *i.e.*, in the neighborhood of the critical point, the following empirical relation holds, according to van der Waals:

$$log\,\frac{\pi_0}{p} = a'\left(\frac{\vartheta_0}{T} - 1\right)$$

According to the theorem of corresponding states, the vapor-pressure curve as well as the equation of state must be a universal function of the reduced quantities, and the constant a' should, therefore, be the same for all substances. Actually, for substances investigated up to the present, it varies between 1.25 (helium) and 4.00 (ethyl alcohol). For a number of liquids which boil between 0 and 100°C., a' varies around the value 3.32.

*Another important rule which depends upon this theorem is that of Ramsay and Young (1885). If two closely related liquids are compared at the same pressures, the following relation holds true:

$$\frac{T_A}{T_B} = \frac{T_A'}{T_B'} = Const.,$$

where T_A and T_B are the boiling points (absolute scale) at one pressure and T_A' and T_B' at a different pressure. A more exact relation is

$$\frac{T_A'}{T_B'} = \frac{T_A}{T_B} + c(T_A' - T_A).$$

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[1] A. Byk (*Ann. Physik*, **66**, 161 (1921), **69**, 157 (1922)) supposes that this fourth constant is Planck's constant h.

The constant c approaches zero when the two liquids are very closely related and is negligible in many cases. It thus may serve as a test of the "normality" or "abnormality" of the liquid.[1]

*Recent investigations have shown that liquids which have been made extremely dry by keeping them in the presence of phosphorus pentoxide for long periods of time have boiling points which are appreciably higher than those of the usual pure liquids.[2] The boiling points for various liquids increased from 14 to 62° and it is peculiar that, while the temperature of the liquid reached these high values, the vapor condensed at the usual temperature. Although the full significance of these results has not yet been determined, they are of utmost importance in the interpretation of the constitution of the liquid state.[3]

The vapor pressure attained at the critical point is the **critical pressure**; since the liquid is no longer capable of existing above the critical temperature, the vapor-pressure curve ends at this point.

According to a rule found by Guldberg, the vapor pressure of many substances reaches atmospheric pressure at about two-thirds of the critical temperature. Thus, $\frac{T_{b.p}}{\vartheta_0} = \frac{2}{3}$, which means that the boiling point $T_{b.p}$ under atmospheric temperature can, in general, be considered as a "corresponding temperature." However, Guldberg's rule has not yet been tested for high boiling substances (metals, salts, etc), so it appears doubtful whether its application to these substances is permissible (*e.g.*, the determination of the critical temperature from the boiling point).

117. The Rule of Cailletet and Mathias.--As a result of the rapid increase of the vapor pressure, the density of the saturated vapor also increases with the temperature. The density of the liquid in equilibrium with the vapor, however, decreases as the temperature rises, for at the critical point the density must be the same for both states. When both densities are plotted as a function of the temperature, a parabolic curve similar to the one for ethyl ether, illustrated in Fig. 29, is obtained. If the arithmetic mean $\frac{\delta_1 + \delta_2}{2}$ is taken and likewise plotted, these points lie on a straight line. The use of this rule discovered by Cailletet and Mathias, that the average density of the liquid and gaseous phases in equilibrium is a straight-line function of the temperature, gives a more accurate method of determining the critical volume than the direct determination from the critical isotherm. This is often called the **law of rectilinear diameters.**

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[1] * For a further discussion of this and other relationships see WASHBURN, "Principles of Physical Chemistry," p. 67, McGraw-Hill Book Company, Inc. (1921), and W McC Lewis, *loc cit*, **1**, p 92

[2] *BAKER, H B, *J Chem. Soc. London*, **121**, 568 (1922).

[3] *LEWIS, G N., *J. Am Chem. Soc.*, **45**, 2836 (1923). SMITS, A, "Theory of Allotropy," p. 316, Longmans, Green & Co. (1922). WILLIAMS and DANIELS, *J. Am. Chem. Soc.*, **47**, 1490 (1925).

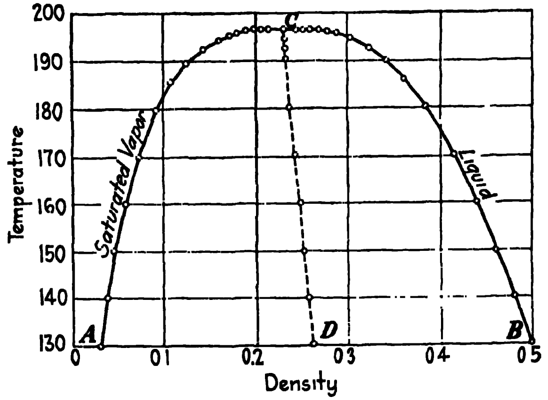

Fig 29

118. Sublimation Pressure.—Below the melting point, solid substances are able to pass directly into the gaseous state *i.e.*, they **sublime.** The process of sublimation is, theoretically, the same as evaporation,[1] but, while the vapor pressure (of liquids) near the critical point can assume very high values, the maximum sublimation pressure, which is reached at the melting point, is frequently of the order of 1 *mm.* of Hg (ice, 4.579 *mm.*) and very often is much less (Hg, $2 \cdot 10^{-6}$ *mm.*). Only for a few substances like carbon dioxide, phosphorus, and arsenic does it exceed atmospheric pressure.

119. The Dependence of the Melting Point on Pressure.—The process of melting, *i.e.*, the transition from the solid to the liquid state, takes place at a definite temperature under a definite pressure. If the pressure acting on the solid is changed, the melting point changes. In this respect the melting point is similar to the boiling point. However, while the boiling point of a liquid is always increased when the pressure is increased, the melting point increases in some cases and decreases in others. As a rule, only small changes of melting point accompany large changes of pressure. For example, benzene melts at +5.43°C. under atmospheric pressure, and at +31°C. at 1000 *atm.* Ice melts under its own vapor pressure at exactly 0°C., but at −0.76° under 100 *atm.*

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[1] * For this reason the term "vapor pressure of solids" is sometimes used.

While the vapor-pressure curve ceases at the critical point, the melting-point curve may be followed up to very high pressures without showing signs of ending. However, liquids and solids become more and more similar as the pressure increases. The difference in the densities of solid and liquid benzene is only half at great at 3000 as at 1 *atm.* From the mode of propagation of earthquake waves through the interior of the earth, it also follows that the liquid magma under the enormous pressures of that region possesses throughout the elastic properties of solid substances. Whether the boundary between solid and liquid is gradually effaced at high pressures, or whether it ceases suddenly at some definite point corresponding to the critical point in the evaporation process, cannot be finally decided as yet According to Tammann's investigations, the first assumption appears to be the more probable one [1]

The transition between different modifications of the solid state also depends on pressure and temperature, *i.e.*, there is a *transition pressure* which, like the *melting pressure*, is a function of the temperature.

120. The Triple Point.—The transition curves (vapor-pressure curve, melting-point curve, etc.) discussed above give the conditions of pressure and temperature under which two phases are in equilibrium.

Under certain conditions, three phases may also be in equilibrium, but this, of course, is possible only at a point representing a definite pressure *and* temperature, and not along a curve. For example, ice, water, and water vapor can coexist only at 0°C. and under the vapor pressure common to both ice and water at this temperature. Thus, at this **triple point** common to all three phases, three transition curves intersect (melting curve, sublimation curve, and vapor-pressure curve).

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[1] * This is a difficult question to decide. From purely molecular-kinetic considerations it is not impossible that the transition from liquid to solid should have the same continuity as from gas to liquid On the other hand, such a transition has never been observed, although Bridgeman has reached pressures of 20,000 *atm.* in his investigations. A discussion of both sides of this question is given by K. JELLINEK, "Lehrbuch der physikalischen Chemie," **2**, p. 640 *et seq.*, Stuttgart (1915).

If a substance has several solid modifications, then there are also several triple points. Typical diagrams illustrating the transition curves and triple points of water and sulfur are given in Figs. 30 and 31, in which the ordinate is the logarithm of the equilibrium pressure. From Fig. 30 it may be concluded that there are modifications of ice which are stable only at very high pressures.

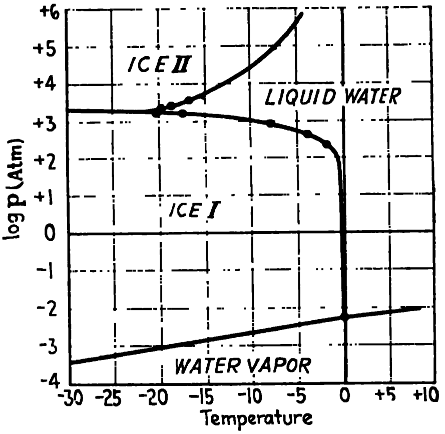

FIG 30

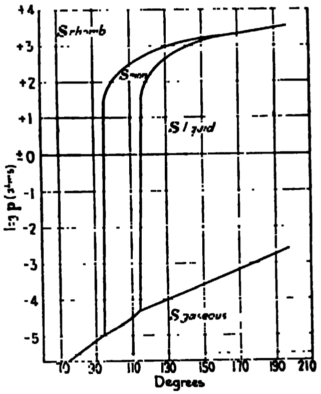

FIG 31

121. Heat of Evaporation.—When a transition occurs from one phase to another, a heat effect is always observed, which is called the **heat of vaporization, of fusion, or of sublimation,** according to the phenomenon involved. The transition from the phase which is stable at the lower temperature to the one stable at the higher temperature is always accompanied by an absorption of heat.

In general, the heat of vaporization Λ varies with temperature (see **126**), but the variation at low and medium vapor pressures is, at most, rather small. Near the critical point, Λ decreases rapidly and at the critical point is zero. If the heats of vaporization for different liquids are compared, it will be seen (Table 20*a*) that, as a rule, the higher the boiling point the greater is the heat of vaporization. Trouton assumed that as a first approximation the molecular heat of vaporization Λ_{bp} at the normal boiling point (1 *atm.*) is proportional to the boiling point on the absolute scale T_{bp}, and put

$$\frac{\Lambda_{bp}}{T_{bp}} \simeq 22. \qquad (125)$$

TABLE 20*a*.—HEAT OF VAPORIZATION AND BOILING POINT

Substance	Λ_{bp} *cal.*	T_{bp}	$\frac{\Lambda_{bp}}{T_{bp}}$ obs.	$\frac{\Lambda_{bp}}{T_{bp}}$ calc.	$\frac{\Lambda_{bp}}{T_{bp}}$ calc. Eq (125*b*)
He	abt 22	4.29	5.1	6.6	6.15
H_2	220	20.4	10.8	11.7	11.8
N_2	1370	77.5	17.6	16.0	17.5
O_2	1620	90.1	18.0	16.5	18.3
CS_2	6490	319	20.4	20.5	20.4
C_6H_6	7400	353	21.0	20.8	20.3
H_2O	9650	373.1	25.9	21.0	25.1
Aniline	9700	157	21.2	21.7	23.3
Hg	14200	630	22.6	22.7	
Na	23300	1155	20.2	24.5	
Zn	27730	1180	23.5	24.6	

As Table 20*a* shows, the ratio $\frac{\Lambda_{bp}}{T_{bp}}$ is by no means constant. Later, von Wartenberg represented the dependence of $\frac{\Lambda_{bp}}{T_{bp}}$ on T_{bp} by the equation

$$\frac{\Lambda_{bp}}{T_{bp}} \simeq 7.4 \log T_{bp} + 1.985, \qquad {}^{*}(125a)$$

but other similarly constructed formulas have also been suggested (Nernst, deForcrand).[1]

In order to obtain an exact expression for $\frac{\Lambda_{bp}}{T_{bp}}$, other specific constants besides T_{bp} must be taken into consideration. As the last column of Table 20*a* shows, the equation

$$\frac{\Lambda_{bp}}{T_{bp}} = \frac{4.571 \log \pi_0}{1 - \frac{T_{bp}}{\vartheta_0}}\left(1 - \frac{1}{\pi_0}\right) \qquad (125b)$$

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[1] * See LEWIS, W. McC., *loc. cit.*, **2**, p. 75 *et seq.*

derived by Cederberg is apparently rather good. The ratio $\frac{\Lambda_{bp}}{T_{bp}}$, according to this equation, depends very much on the critical pressure π_0. Since this quantity is closely related to the constant b (see Eq. (121)), which is a measure of space occupied by the atoms, it is clear that substances with large atomic volume (see **261**) should show abnormally small values of $\frac{\Lambda_{bp}}{T_{bp}}$ (Na, 20.2; K, about 19; Rb, about 17.5), while substances with relatively small b (small atomic or molecular volumes) should have large values for the ratio. Relatively high values of Λ_{bp}, and, therefore, also for the ratio, are to be expected if the substance polymerizes into larger molecules in the liquid state, since in such a case the heat of evaporation includes a heat of depolymerization. Whether the high value of the ratio for H_2O is due mostly to the influence of polymerization, which is certainly present, or to the relatively small value of b is still in doubt.

*Hildebrand[1] gives an important rule involving the entropy of evaporation, *i.e.*, the heat of vaporization divided by the temperature at which the vaporization takes place. In order to represent the entropy graphically, Eq. (131*a*) (see **129**) is put into the form

$$\frac{d\ log\ p}{d\ log\ T} = \frac{\Lambda}{RT}. \qquad (131h)$$

Now $\frac{\Lambda}{T}$ is the entropy, so that, if *log p* be plotted against *log T*, the tangent to the curve at any point is equal to the entropy divided by *R*. By plotting a number of such curves, it was found that the points where their tangents had the same slope were on a straight line which could be represented by $log\ p = log\ T + K$, where K is a constant. If the vapor obeys the gas laws, then $p = cRT$ and $log\ p = log\ T + log\ Rc$, therefore $K = log\ Rc$, and along such a line the concentrations must be constant. Hildebrand therefore states that: "*the entropy of vaporization for normal liquids is the same when evaporated to the same concentration, i.e., when the final mean distance between the molecules of vapor is the same.*" It must be emphasized that Trouton's rule makes the comparison at constant pressure (1 *atm.*) and not at constant concentration, and under constant-pressure conditions the entropies are not the same. In order to compare the results by the two different rules, the following table shows the values of $\frac{\Lambda}{RT_{conc}}$ at constant concentration, and $\frac{\Lambda}{RT_{pr}}$ at constant pressure with the corresponding temperatures T_{conc}. and T_{pr}.[1]

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[1] * *J. Am. Chem. Soc*, **37**, 970 (1915), **40**, 45 (1918).

TABLE 20b—COMPARISON OF HILDEBRAND'S AND TROUTON'S RULES

Substance	$\frac{\Lambda}{RT_{conc}}$	$\frac{\Lambda}{RT_{pr}}$	T_{conc}	T_{pr}
N_2	13 8	11 0	55	63
O_2..	13 8	11 4	75	81
Cl_2. .	13 9	13 5	194	200
Pentane .	13 5	13 2	256	260
CCl_4.	13 5	13 4	294	295
C_6H_6 .	13 7	13 7	298	299
Hg...	13 1	13 5	560	533
Cd.	13 2	14 8	988	908
Zn.	13 2	15 1	1130	1030
NH_3	16 2		200	
H_2O .	16 0		325	
C_2H_5OH	16 7		307	

*This table shows that for normal substances $\frac{\Lambda}{RT_{conc}}$ is considerably more constant than $\frac{\Lambda}{RT_{pr}}$ and, further, that it does not vary systematically with temperature. The effect of association on the constant is indicated by the last three values.

122. Heat of Fusion and Melting Point.—The heat of fusion is considerably (about ten times) smaller than the heat of vaporization at the boiling point, at least for substances which, in the sense of **61** and **76**, may be considered as simple monoatomic solids. A relation analogous to Trouton's rule between the atomic heat of fusion Λ_f and the melting point T'_{mp} is thus found to be

$$\Lambda_f = \text{approx. } 2\ 2\ T'_{mp}. \qquad (126)$$

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[1] * The value of log Rc in column 2 is -0 5 corresponding to a concentration of .00507 moles of vapor per l. In column 3, log p = 2.0, p being expressed in *mm.* Hg.

As Table 21 shows, a marked change of the ratio $\frac{\lambda_f}{T'_{mp}}$ with temperature is not discernible in this case, as in Trouton's constant. Relatively small differences in the value of this ratio are found when the elements are chemically related (*e.g.*, K, Na, Cu, Ag).

TABLE 21.—HEAT OF FUSION AND MELTING POINT

Substance	λ_f	T'_{mp}	$\frac{\lambda_f}{T'_{mp}}$
Ar	368	83.8	3.2
Hg	564	234	2.35
K	625	335	1.87
Na	730	370	1.97
Pb	1150	600	1.92
Zn	1830	691	2.65
Cd	1570	594	2.65
Al	2080	930	2.23
Ag	2370	1233	1.92
Cu	2730	1356	2.02

123. Transition Velocity (Velocity of Crystallization).—The velocity with which one phase transforms into another depends entirely upon the rate at which heat is added or removed, provided the two phases were in equilibrium initially. For instance, a liquid at constant temperature can be evaporated only as fast as the heat necessary for its evaporation is added. The velocity of growth of a single crystal, in its melt, along a definite direction (the so-called linear velocity of crystallizaton) depends altogether on the speed with which the heat set free in the process is conducted away from the crystal. This is true at least in the vicinity of the melting point.

If the addition or the removal of heat is sufficiently rapid, the transition from one phase to another usually takes place without delay, provided a certain amount of the phase to be formed is present. An exception to this rule is the crystallization of liquids (glasses) which are cooled far below their solidification point (*i.e.*, they are "supercooled"). Such liquids in all cases crystallize with extreme slowness. The transition from one crystal phase to another in the solid state is also an exceedingly slow process and in many cases great patience is required in order to determine even the direction in which the transformation is taking place. In other cases, however, these transitions among allotropic modifications take place rapidly and, strange to say, even at very low temperatures. For example, in the transition between the solid forms of oxygen at 23.5 and 42.5° *abs.* only slight delay has been observed.

The transition may be considerably delayed, if only one of the phases is present in the beginning, *i. e.*, the transition point (boiling point or crystallization point) may be considerably exceeded without the formation of the new phase. In the liquid-gas transformation it is thus possible to follow along the branches *FM* and *GN* of the curve in Fig. 27. In these cases the substance is said to be a supersaturated vapor or a superheated liquid. On the other hand, an overheated solid has never been observed with certainty.

The delay in the transition, which under the proper conditions, may continue for a long time, can often be rapidly removed by various external influences. One of the best ways is to introduce a small amount of the desired phase. For example, crystallization can often be started by "inoculating" the melt with a tiny crystal of the new phase. Superheating a liquid can usually be avoided or removed by any sort of small gas bubbles. In other cases the presence of foreign substances is sufficient to prevent the delay. For supersaturated water vapor (also other vapors) the presence of dust particles or even gas ions which will serve as condensation nuclei causes water drops to form immediately.

Especially interesting are those cases in which the new phase suddenly appears after a time, without any visible external assistance. Since it is relatively easy to cool a number of melted solids very much below the crystallization point (the phenomenon is, of course, limited to substances of rather high molecular complexity), the circumstances under which the transition liquid-to-solid (crystallization) takes place spontaneously could be investigated with some degree of accuracy. The result was as follows: Upon cooling below the crystallization point, crystal "nuclei," or centers from which crystallization spreads out, are first formed in the undercooled liquid. In many cases the velocity with which these nuclei form is very small just below the melting point, increases as the temperature drops, passes through a maximum, and by still further undercooling decreases to zero. The presence of the nuclei does not necessarily lead directly to the formation of crystals. At sufficiently low temperatures the nuclei remain latent—in general, this is the case when the liquid is very viscous—and only when the temperature is again increased, perhaps up close to the melting point, do the nuclei begin to grow into visible crystals. If the velocity of formation of these nuclei is sufficiently large just beneath the melting point, then the nuclei do not remain latent but grow immediately into visible crystals. The velocity of this nuclei formation depends, to a high degree, upon secondary influences. It is always reduced by the presence of slight amounts of impurities.

On the whole, the velocity with which a crystal of a solid substance forms from its melt is largely determined by two factors: (1) the velocity with which the centers of crystallization form spontaneously; (2) the linear velocity of crystallization. The ratio of these two factors determines whether the crystals of the solidified substance will be large or small.

Interesting investigations on the velocity of formation of crystals from vapors (in extremely low concentration) have been performed by M. Vollmer,[1] which seem to give a very much better insight into the real mechanism of crystal growth than the investigations upon solutions and melts.

b. THERMODYNAMIC RELATIONS

124. Equilibrium between Several Phases.—The empirical fact that a solid or a liquid substance at any given temperature has a definite vapor pressure may be considered as a necessary consequence of the Second Law. Assuming that a liquid could be in equilibrium with its vapor at various pressures (at the same temperature), it could then be evaporated at a higher pressure, next perform work by expanding, and, finally, be condensed at a lower pressure into liquid. Since this process could be repeated as often as desired, any amount of work could be performed at the expense of the heat of the surroundings, or, in other words, a perpetual motion of the second class would be realized.

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[1] *Z. Physik*, **5**, 31, 188, **7**, 1, 13 (1921).

In a similar way, thermodynamics requires that three phases can be in equilibrium only at a definite point, the triple point, or, what amounts to the same thing, that the three transition curves must always intersect at one point. If the sublimation pressure at the melting point were higher than the vapor pressure of the liquid, then the solid would sublime continuously and condense as a liquid. A transition from the solid to the liquid state would take place through the gas phase, a process which could be used to perform work. The liquid thus formed can again be converted directly into the solid state without the performance of work (since the melting point is defined as the equilibrium point between the solid and liquid phases), so that the system would revert completely to its original state and yet have performed work. In order to remove the possibility of a perpetual motion of the second class, it is necessary that the vapor pressure of the liquid and the solid be equal at the melting point. Three transition curves must, therefore, intersect in one point, which is in agreement with experimental results.

It will be seen at once that the sublimation curve must have a steeper slope than the vapor-pressure curve, *i.e.*, $\left(\frac{dp}{dT}\right)_{sub} > \left(\frac{dp}{dT}\right)_{evap}$. In every case, that phase is stable which has the lower vapor pressure. This results from the following consideration: If two phases which have different vapor pressures exist together, then in the course of time the phase with the lower vapor pressure will increase at the expense of the other,[1] *i.e.*, the phase with the higher vapor pressure is unstable. Since the liquid is unstable below the freezing point, it has a higher vapor pressure than the solid. It follows that the prolongation of the vapor-pressure curve for the liquid below its freezing point must lie above the sublimation curve and therefore have a less steep slope than the latter (see Fig. 36).

125. Heat of Vaporization and External Work.—Since a transition usually involves the performance of a certain amount of work against external pressure, it is frequently convenient to divide the total thermal effect Q into external work performed, and change of internal energy:

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[1] * This is simply a distillation from higher to lower pressure at constant temperature.

$$Q = U + A.$$

In the above case Q corresponds to the total heat of vaporization Λ; U to the internal heat of vaporization Λ_i; and A is the external work performed.

Since this change of state is a process taking place under constant pressure, then from Eq. (44a):

$$A = p\int_{v_2}^{v_1} dv = p(v_1 - v_2) = p\Delta v,$$

in which v_1 is the volume of the new phase, v_2 that of the disappearing phase, and Δv the difference between the two. In the special case of vaporization at low pressures, v_2 is very small in comparison with v_1 and may, therefore, be neglected. At the same time, as long as the vapor approximately obeys the gas law, we have, for low pressures,

$$A = pv_m = RT,$$

so that, finally,

$$\Lambda = \Lambda_i + RT. \qquad (127)$$

At room temperature the work RT amounts to about 600 *cal.*; the heat of vaporization according to Trouton's rule (**121**) is about 6600 *cal.* The difference between Λ and Λ_i is thus about 10 per cent.

126. The Relation between Heat of Vaporization and Temperature.—A simple relation between the dependence of heat of vaporization upon temperature and the specific heat may be obtained by the following consideration: The system liquid-vapor is first at the temperature T and is then heated at constant volume to $T + dT$. In the heating process not only the heat required to warm the gas (as determined by the specific heat) must be added, but also a certain amount necessary to evaporate a portion of the liquid, since the vapor pressure has increased. Let the volume ratio be so chosen that just one mole is evaporated. The heating and the evaporation may be imagined to take place in steps: First heat the liquid to the temperature $T + dT$ without evaporating any of it; it is thus in a superheated state. For this purpose the heat $C'_{p_2}dT$ is necessary. (This statement is not quite correct, since the pressure in the gas space is not constant, but slightly increases due to the temperature increase.) The superheated liquid is then evaporated at the temperature $T + dT$ *without* performing work, *i.e.*, the internal heat of vaporization $\Lambda_i + d\Lambda_i$ is consumed. The system is now cooled again by first undercooling the vapor, thus setting free the heat $C_{v_1}\,dT$, neglecting the trifling contraction in the volume of the liquid. Finally, the gas is condensed at the temperature T by which the quantity of heat Λ_i is liberated and the system is back in its original state.

From the First Law it is obvious that the sum of all the absorbed and liberated energies in the process must be zero, since otherwise the construction of a perpetual motion of the first kind would be conceivable. Thus (by disregarding some trifling quantities) the relation

$$C'_{p_2}dT + \Lambda_i + d\Lambda_i - C'_{v_1}dT - \Lambda_i = 0$$

or

$$\frac{d\Lambda_i}{dT} = C'_{v_1} - C'_{p_2}. \tag{128}$$

If it is assumed that the ideal gas law holds for vapors, then $C'_{p_1} - R$ may be substituted for C'_{v_1} (Eq. (77)) and $\Lambda - RT$ for Λ_i (Eq. (127)), so that for the total heat of evaporation we finally get

$$\frac{d\Lambda}{dT} = C'_{p_1} - C'_{p_2}. \tag{128a}$$

However, it must once more be emphasized that this relation is not rigorous but contains several simplifying assumptions, namely, that the specific volume and the compressibility of the liquid are small in comparison with that of the gas, and that the ideal gas law is applicable to vapors. If it is not permissible to make these assumptions, a correction term must be added to the right side of Eq. (128a), amounting to

$$+\frac{dp}{dT}\left\{(v_1 - v_2) - T\left(\frac{\partial v_1}{\partial T} - \frac{\partial v_2}{\partial T}\right)\right\}$$

$\left(\frac{dp}{dT}\right.$ is the increase of vapor pressure with temperature$\left.\right)$

As a test of Eq (128a), some experimental values for $\frac{d\Lambda}{dT}$ and $C_{p_1} - C_{p_2}$ are compared in Table 22, columns 4 and 7. This shows that the simplified

Eq. (128a) is satisfied by the experimental results for water vapor only at a pressure of about $^1\!/_{10}$ atm, where the accuracy is approximately 2 per cent. At atmospheric pressure the deviation is already more than 20 per cent.

TABLE 22.—APPLICATION OF EQ (128a) TO WATER VAPOR

T	p atm	Λ (cal.)	$\frac{d\Lambda}{dT}$	C'_{p_1}	C'_{p_2}	$C'_{p_1} - C'_{p_2}$
313	0.072	10350	−9.8	8.20	18.00	−9.80
333	0.196	10160	−10.3	8.24	18.05	−9.81
353	0.477	9940	−10.8	8.28	18.10	−9.82
373	1.0	9720	−11.5	8.32	18.15	−9.83

127. Heats of Sublimation, Fusion, and Vaporization.—On the basis of the energy principle, we must have at the melting point:

$$[\Lambda_{1,3}]_{mp} \text{ (heat of sublimation)} = [\Lambda_{1,2}]_{mp} \text{ (heat of vaporization)} + [\Lambda_{2,3}] \text{ (heat of fusion)}, \qquad (129)$$

because the energy involved in the conversion of a solid substance into a gas must be the same whether the conversion takes place directly, or indirectly through the liquid state

Equation (128a), which, obviously, is just as applicable to the sublimation as to the evaporation process, upon integration up to the melting point T_{mp}, gives

$$[\Lambda_{1,3}]_{mp} = \Lambda_0 + \int_0^{T_{mp}} (C'_{p_1} - C'_{p_2})dT \qquad (130)$$

and, further,

$$\Lambda_{1,2} = [\Lambda_{1,2}]_{mp} + \int_{T_{mp}}^{T} (C'_{p_1} - C'_{p_2})dT,$$

if Λ_0 is the heat of sublimation at the absolute zero and the index mp refers to the melting point. Therefore, with respect to Eq. (129) we get

$$\Lambda_{1,2} = \Lambda_0 + \int_0^{T_{mp}} (C'_{p_1} - C'_{p_2})dT - \Lambda_f + \int_{T_{mp}}^{T} (C_{p_1} - C_{p_2})dT. \qquad (130a)$$

Accordingly, it is possible to calculate the heat of vaporization or sublimation of a substance accurately at any temperature as long as the pressures are small (*i.e.*, Eq. (128a) is valid) and provided the heat of sublimation at the absolute zero, the heat of fusion, and the change of specific heat of the solid, liquid, and gas with temperature are known.

128. The Clapeyron-Clausius Equation.—For the relation between the equilibrium pressure of two phases and the temperature, and, in particular, the relation between the vapor pressure of solid or liquid substances and temperature, the First and Second laws give a formula which is of fundamental importance. This was first derived by Clapeyron (1834) on the basis of Carnot's "material" heat theory,[1] and later by Clausius on the basis of the modern (mechanical) theory. The formula thus bears the name of both men.

The Clapeyron-Clausius equation, like many thermodynamic formulas, refers back to the fundamental Eq. (19), from which it may be derived directly by considering a cyclic process in which heat is reversibly transferred by evaporating a liquid in a warmer heat reservoir at the vapor pressure p, and condensing the vapor into a colder reservoir at the vapor pressure $p - dp$.

For the performance of such a cyclic process a fusion or transition between two allotropic states can be used quite as well as a vaporization process. If the process is limited to a very small temperature difference dT between the two heat containers, then, similar to the derivation of Eq. (51), the heat transported directly due to the heat capacity of the substance can be neglected. The heat Q_r then corresponds directly to the heat of evaporation Λ (see **125**).

As the total amount of work obtainable from this process we have $dA = dp(v_1 - v_2)$, in which dp is the increase in pressure corresponding to the temperature increase dT, and $(v_1 - v_2)$ is the difference between the molecular volumes of the vapor and the condensate. If this value is put in Eq. (49), the Clapeyron-Clausius equation results.[2]

$$\Lambda = T\left(\frac{dp}{dT}\right)(v_1 - v_2) \quad \text{or} \quad \frac{dp}{dT} = \frac{\Lambda}{T(v_1 - v_2)}. \qquad (131)$$

The consideration of a special cyclic process is unnecessary if Eq. (51) is applied, since this equation is obtained from a general cyclic process. The maximum work A_T performed in an isothermal evaporation (since the pressure is also constant) is given by

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[1] See footnote to **19**.

[2] For more details the reader should consult LEWIS, G. N. and RANDALL, M., *loc cit*, p. 181, MACDOUGALL, *loc cit.*, p. 128, SACKUR, "Thermochemistry and Thermodynamics," p. 209, Macmillan Company, translated by GIBSON.

$$A_T = p\,(v_1 - v_2).$$

It follows, therefore, that

$$\left(\frac{\partial A_T}{\partial T}\right)_v = \frac{dp}{dT}(v_1 - v_2),$$

since p is independent of the volume, and the partial differential $\left(\frac{\partial p}{\partial T}\right)_v$ can thus be replaced by the total.

This again leads directly to Eq. (131).

129. The Behavior of the Vapor-pressure Curve.—If the Clapeyron-Clausius equation is applied to the evaporation (or sublimation) process, it will be found possible to calculate the heat of vaporization from the change of vapor pressure with temperature.

As an example, the heat of vaporization of water, for which the vapor pressure has been measured very accurately, may be calculated. The vapor pressure at 99.9°C. is 757.29, at 100 1°C., 762.72 *mm.* Hg. The differential coefficient is thus very nearly $\frac{dp}{dT} = \frac{762.72 - 757.29}{0.2} = \frac{5.43}{0.2} = 27.15$ *mm.* Hg $= 0\ 03575$ *atm.* per degree. The volume of a mole of water vapor at 373.2° *abs.* is 18.01 × 1.6505 *l.*; that of a mole of the liquid is 18.01 × 0.001043. Then from Eq. (131) we get $\Lambda = 373.2 \times 0.03575 \times 18.01 \times 1.649 = 396.2$ *l.-atm.* = 9590 *cal.*, while the directly determined calorimetric value is 9650 *cal.*

However, what is more important than the calculation of the heat of vaporization is the circumstance that this formula, even though it has a differential form, represents an exact equation for the vapor-pressure curve. In order to integrate it, the temperature function of both $v_1 - v_2$ and Λ must, of course, be known and, in general, cannot be presupposed. For small pressures, however, some simplifications are permissible. In the first place v_2 (liquid) can be neglected in comparison with v_1 (gas) and v_1 can be replaced by $\frac{RT}{p}$.

Thus, Eq. (131) transforms into

$$\frac{1}{p}\frac{dp}{dT} = \frac{d\,ln\,p}{dT} = \frac{\Lambda}{RT^2}, \qquad (131a)$$

from which, on integrating,

$$ln\ p = \int \frac{\Lambda}{RT^2} dT + Const., \qquad (131b)$$

or, integrating over the temperature interval T_1 to T_2,

$$ln\ p_2 - ln\ p_1 = ln\ \frac{p_2}{p_1} = \int_{T_1}^{T_2} \frac{\Lambda}{RT^2} dT. \qquad (131c)$$

If Λ is independent of the temperature, it follows that

$$ln\ \frac{p_1}{p_2} = \Lambda \frac{T_1 - T_2}{RT_1T_2}. \qquad (131d)$$

Even when Λ varies with temperature, Eq. (131*a*) may still be frequently used, provided the temperature interval is relatively small. If it is attempted to apply this equation directly to large temperature intervals, a value of Λ is obtained which does not agree with that of the mean value $\frac{T_1 + T_2}{2}$ but that of some lower temperature. If, for example, the values for water vapor are substituted as follows: $p_1 = 1$ *atm.*, $p_2 = 0.00603$ *atm.*, $T_1 = 373.2°$, $T_2 = 273.2°$, the value obtained for Λ is 10320 *cal.*, which is the correct value for $T = 313°$ and not for that of the mean temperature 323.2°.

In order to evaluate the integral Eq. (131*b*) over a large temperature interval, we must turn back to Eq. (128*a*) or Eq. (130) and be limited to the vaporization of solid substances.

By introducing Eq. (128*a*) or Eq. (130) into Eq. (131*b*) the following formula is obtained:

$$ln\ p = -\frac{\Lambda_0}{RT} + \int \frac{\int_0^T (C'_{p_1} - C'_p)dT}{RT^2} \cdot dT + Const, \qquad (131e)$$

which, in general, holds good only for small pressures (where the ideal gas law is applicable to vapors).

The indefinite integral in Eq. (131*b*) must again be replaced by a definite integral so that the integration constant also acquires a definite numerical value. To do this, C'_{p1} is resolved into one constant part (C'_{p_0}) and one part (C_T') which is dependent on the temperature and is due to the energy of molecular vibration and perhaps also rotation. The part of the integral in Eq. (131*e*) which corresponds to C_{p_0} is then simply equal to $\frac{C'_{p_0}}{R} ln\ T$.

Now, since at very low temperatures C_{p_3} is proportional to T^3, and C'_T (assuming the validity of the Einstein function Eq. (98*a*) or a similar relation) in any case decreases more rapidly than T, not only the integral $\int_0^T (C'_{T'} - C'_{p_3})dT$ but also the expression $\int \frac{dT}{T^2}\int_0^T (C'_{T'} - C'_{p_3})dT$ vanishes for $T = 0$. It is an advantage to choose the value $T = 0$ as the lower limit of the previously indefinite integral (the upper limit retains the variable value T). In place of the undetermined constant (*Const.*), a fixed numerical value, which is designated by the symbol i, will be used in the following.

Finally, if ordinary logarithms are substituted for the natural ones and $R = 1.985$ *cal.*, the vapor-pressure formula takes the form

$$\log_{10} p = -\frac{\Lambda_0}{4.571T} + \frac{C_{p_0}}{1.986}\log_{10} T + \frac{1}{4.571}\int_0^T \frac{dT}{T^2}\int_0^T (C'_{T'} - C'_{p_3})dT + i, \qquad (131f)$$

in which it will be used later in the exact thermodynamic calculation of the chemical equilibrium (see **225**).

130. The Vapor-pressure Curve of Liquids.—In order to obtain the vapor-pressure curve for a liquid, Eq (130*a*) is to be substituted in Eq (131c) and the integration performed between the melting point T_{mp} and any other temperature T. It then follows that

$$\log p - \log p_{mp} = \int_{T_{mp}}^{T} \frac{\Lambda_0 + \int_0^{T_{mp}} (C'_{p_1} - C'_{p_3})dT - \Lambda_{2,3} + \int_{T_{mp}}^{T} (C'_{p_1} - C'_{p_2})dT}{4.571T^2}\, dT.$$

Since the vapor pressures of the liquid and solid phases must be the same at the melting point, $\log p_{mp}$ in this equation may be replaced by the value given for it by Eq (131*f*), while T is put equal to T_{mp} everywhere except in the internal integral. In this way the following equation is finally obtained

$$\log p = -\frac{\Lambda_0}{4.571T} + \frac{C_{p_0}}{1.986}\log T + \frac{1}{4.571}\int_0^T \frac{dT}{T^2}\int_0^T C'_{T'}dT$$

$$-\frac{1}{4.571}\int_0^{T_{mp}} \frac{dT}{T^2}\int_0^T C'_{p_3}dT$$

$$-\frac{1}{4.571}\int_{T_{mp}}^{T} \frac{dT}{T^2}\left(\int_0^{T_{mp}} C_{p_3}dT + \Lambda_{2,3} + \int_{T_{mp}}^{T} C'_{p_2}dT\right) + i. \qquad (132)$$

For the case where it is permissible to put $C''_T = 0$ and $C_{p_2} = \text{Const.}$, which occurs quite often, the following is obtained after several transformations:

$$log\ p = -\frac{\Lambda_0'}{4.571T} + \frac{C_{p_0} - C_{p_2}}{1.986}\ log\ T + C'', \tag{132a}$$

where

$$\Lambda_0' = \Lambda_0 - \Lambda_{2,3} - C_{p_2}T_{mp} + \int_0^{T_{mp}} C_{p_3}dT \tag{132b}$$

is the *extrapolated* heat of vaporization of the liquid at the absolute zero and all the terms independent of temperature are summed up in the constant.

$$C'' = -\frac{1}{4.571}\int_0^{T_{mp}} \frac{dT}{T^2}\int_0^T C_{p_3}dT - \frac{1}{4.571T_{mp}}\left(\Lambda_{2,3} + \int_0^{T_{mp}} C_{p_3}dT\right)$$
$$- \frac{C_{p_0} - C_{p_2}}{1.986}\ log\ T_{mp} + \frac{C_p}{4.571} + i \tag{132c}$$

131. The Chemical Constant.—It is obvious that the absolute value of the vapor pressure can be stated only if the integration constant i is known. Because of its importance in the calculation of the equilibrium of the chemical gas reactions, this constant is generally known as the **chemical constant.** In order to determine this *theoretically*, it is necessary to turn to kinetic considerations, since the thermodynamic laws are not able to say anything about it. In spite of the completely different methods with which the various investigators[1] have attacked the problem, they all agree in giving the following formula for monoatomic substances:

$$i = log_{10} \frac{(2\pi)^{3/2}k^{5/2}}{\mathbf{N}^{3/2}h^3} + \frac{3}{2}\ log_{10} A, \tag{133}$$

in which, except for the atomic weight A, all the quantities are universal constants and, what is even more noteworthy, the Planck quantum of action, which is so important for many atomic processes, also appears. If the numerical values of the constants are introduced and p in Eq. (131*f*) is expressed in atmospheres, then

$$i = -1.587 + 1.5\ log_{10} A. \tag{133a}$$

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[1] SACKUR, O., Nernstfestschrift, p. 405 (1912), *Ann. Physik.* **40,** 67 (1913). TETRODE, H., *Ann Physik.* **38,** 434; **39,** 255 (1912), *Amst. Proc.*, **17,** 1167 (1915). STERN, O., *Physik Zeit*, **14,** 629 (1913). EHRENFEST, P., and TRKAL, V., *Ann Physik.* **65,** 609 (1921). See the article in "Ergebnisse der exakten Naturwissenschaften," **1,** 145 *et seq*, Berlin (1922) and also footnote to **222.**

It is possible to derive an analogous formula for polyatomic molecules, but this involves the main moment of inertia of the molecule as well as the atomic weight. Since in many cases this moment of inertia is not accurately known, the formula has but little practical value at present.[1]

In order to determine i empirically according to Eq. (131*f*) and thus test the theoretical Eq. (133), it is necessary to have a knowledge of the vapor pressure and heat of vaporization at one temperature T, and the change of the molecular heat of the vapor and condensate with temperature between 0 and $T°$. The heat of sublimation at $T = 0$, which appears in Eq. (131*f*), is obtained from Eq. (130). If the molecular heat of the gas is not accurately known in the vicinity of absolute zero, an extrapolation of the values determined at higher temperatures must suffice. In any case it must be remembered that neither Λ_0 nor i represent true values but have only the significance of extrapolated values. In an actual calculation, the necessity of using a value of Λ_0 found by extrapolation instead of a directly determined value never makes an important difference in the final result. For i, even when it is to be applied at high temperatures, such as to the calculation of chemical equilibria, the use of an extrapolated value is of minor importance, provided that the same value of C'_{p_0} (for the gas) upon which the determination of i was based, is used at the same time

For a number of substances the integration constants i can be determined by the methods just described. The values found are given in Tables 23 and 24, in which the limiting value of C'_{p_0} used in the calculation of i from Eq. (131*f*) is also given. The value for H_2 in Table 24 can be used only at high temperatures.

If the vapor-pressure curve of the liquid is followed below the freezing point down to the absolute zero by delaying the crystallization, then Eq. (131*f*) can, obviously, be retained unchanged in form for the liquid. In this case Λ_0 becomes the heat of vaporization of the liquid at absolute zero and C'_{p_s} is to be replaced by C'_{p_l}.

On the basis of the Nernst Heat Theorem (see **224**) it may be shown that, according to this method of treatment, the chemical constant of the liquid has the same value as that of the solid. Even if the substance exists in several solid forms, its chemical constant retains the same value throughout. Therefore, the general statement may be made that the chemical constant of every substance has a definite value which is independent of the nature of the condensate.

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[1] * See, however, the article by H. C. Urey, *J. Am. Chem. Soc.*, **45**, 1445 (1923). References to the works of Tolman, Latimer, Eastman, and others are also to be found there.

TABLE 23.—INTEGRATION CONSTANTS (CHEMICAL CONSTANTS) FOR MONOATOMIC SUBSTANCES[1]

$$C_{p_0} = \tfrac{5}{2}R$$

Substance	i obs.	i calc.
H_2[2]	−1.11 ±0.10	−1.14
Ar	+0.79 ±0.06	+0.81
Zn	+1.15 ±0.05	+1.18
Cd	+1.52 ±0.05	+1.49
Hg	+1.83 ±0.03	+1.86

[1] See also SIMON, F. Z. physik. Chem., **110**, 572 (1924).

[2] According to its thermal behavior at low temperatures (see **52**) the molecule H_2 may be considered as monoatomic.

TABLE 24.—INTEGRATION CONSTANTS (CHEMICAL CONSTANTS) FOR POLYATOMIC SUBSTANCES[1]

Substance	i obs.	C_{p_0} (calc.)
NO	+1.5	6.96
O_2	+0.7	6.96
N_2	0	6.96
CO	0	6.96
CO_2	+0.9	6.96
NH_3	−2.2	8.04
H_2O	−2.1	7.95
H_2	−3.7	6.96

[1] See also EUCKEN, A., Z. Physik, **29**, 1 (1924).

*However, in the more recent work of Simon,[1] and of Gibson and Giauque[2] on the specific heat of glycerine, it has been found that the specific-heat curve of this substance shows a sudden increase at about 180° *abs.*, the point of softening of the supercooled liquid.

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[1] * *Ann. Physik*, **68**, 241 (1922).

[2] * *J. Am. Chem. Soc.*, **45**, 93 (1923).

*The latter authors interpret their results as indicating that at the absolute zero the entropy of a supercooled liquid is greater than that of the crystalline solid, since the specific-heat curve of the crystals does not show the same phenomenon at 180° *abs.* Inasmuch as the entropies in the two states are not the same, it would appear that their chemical constants must be slightly different. This supports the earlier statements of Lewis and Gibson,[1] who claim that the Heat Theorem can hold rigidly only for perfect crystals and not for solutions and liquids.

132. Application of the Clapeyron-Clausius Equation to the Fusion Process.—The Clapeyron-Clausius equation can be applied to the fusion of substances as well as to the evaporation and sublimation, but in this case no simplifications are possible. Several examples of this application of the formula are given in Table 25, in which the change of melting point under a pressure of 100 *atm.* was calculated according to the following equation:

$$\Delta T = \frac{T(v_2 - v_3)\Delta p}{\lambda_{2,3}}. \tag{131g}$$

Since the volume of the liquid is sometimes smaller than that of the solid (H_2O, Bi), the term $(v_2 - v_3)$ becomes negative and in such cases a decrease of the melting point is observed as the pressure increases. In general, however, an increase is found.

TABLE 25

Substance	T	Heat of fusion, calories per gram[1]	$(v_2 - v_3)$ 10^3 cubic centimeters per gram	ΔT for 100 *atm.*	
				Calc.	Obs.
Sn	504	14 25	3 894	0 334	0 328
Cd . .	593	13 70	5 64	0 591	0 629
Pb	600	5 37	3 076	0 832	0 803
Bi..	544	12 6	− 3 42	−0 357	−0 356
H_2O	273 2	79 67	− 9 10	−0 755	−0 76
C_6H_6	278 4	30 6	13 01	2 860	2 90

[1] When used in Eq (131*g*), the heat of fusion must be expressed in *cc atm* (see Table 1)

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[1] * *J. Am Chem. Soc.*, **42**, 1529 (1920).

c. KINETIC THEORY

133. The Equilibrium: Liquid-gas.—The transition between any two phases, as has been shown above, may be treated uniformly by thermodynamic means, but from the kinetic viewpoint very considerable differences develop.

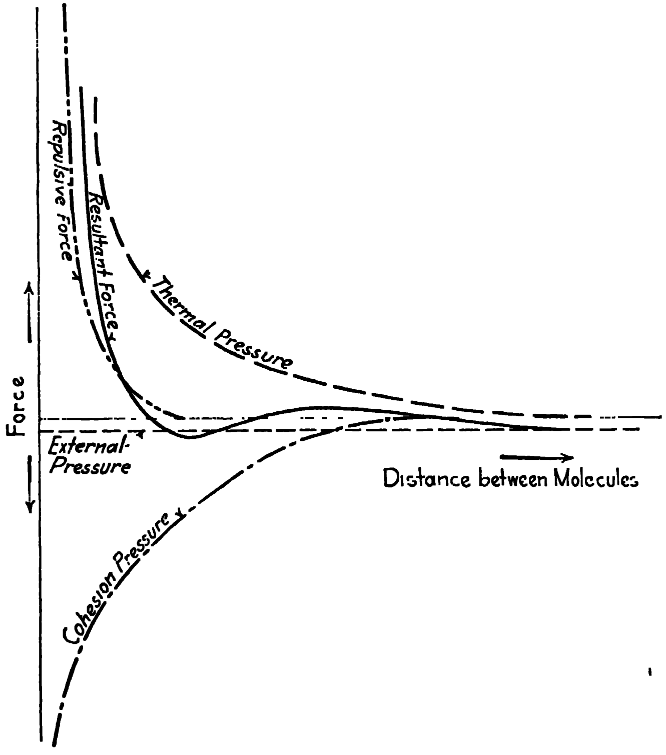

FIG. 32

Qualitatively, the equilibrium, liquid-gas (or solid-gas), may be explained kinetically as a balance set up between all the forces acting on the molecule similar to that discussed in **106**. For this purpose it is only necessary to represent the various pressures (repulsive, attractive, thermal, and external pressures) which act upon the molecule as a function of the molecular distance or volume (Fig. 32). The resulting force, which is represented by the solid line, generally intersects the zero axis three times, *i.e.*, in three places no force is acting upon the molecule. Of these three intersections, only the first and third correspond to positions of stable equilibrium,[1] the first represents the liquid, the third the gas. In order that both liquid and gas should exist together, it is obvious that both equilibrium positions must be equally stable. Otherwise, due to accidental fluctuations in the forces, all the molecules would gradually migrate to the more stable position, just as a stable mechanical equilibrium upon being shaken can finally be shifted into a still more stable equilibrium. The two phases are to be called equally stable when, on the average, as many molecules go from the first phase to the second as in the opposite direction. This is by no means always the case, and, in fact, it happens only when the four forces are equalized in a definite way. The zero line in Fig. 32 must be so placed that, on the average, just as many liquid molecules can exceed the molecular attraction (the minimum of the total force) as gaseous molecules can exceed the small maximum. At a given temperature this is possible only at a definite external pressure. If this pressure is decreased, the maximum becomes higher and thus the third position (gas state) becomes relatively more stable, *i.e.*, the substance evaporates. If the pressure is increased, the maximum decreases and the transition to the liquid state is favored. This explains why liquid and vapor can coexist only at a definite external pressure.

134. The Vaporization Process.—The mechanism of the vaporization process itself may be imagined as follows: The majority of liquid molecules which approach the surface at a certain velocity from the interior are checked by the attractive force of the other molecules and forced to turn back. Only those molecules which reach the surface with an abnormally high velocity can pass through this zone of attraction with sufficient velocity to get out into the gas space. From the other side, all the gas molecules rushing towards the liquid surface come within the range of the attractive force and are drawn into the liquid. The condition of dynamic equilibrium demands that as many molecules evaporate as condense.

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[1] It will be remembered that the second root of van der Waals' equation likewise corresponds to an unstable state.

The number of molecules with velocities sufficiently great to pass the zone of attraction is given theoretically by the Maxwell distribution law, which can be claimed to hold for liquids as well as gases. Figure 13 shows that the number of molecules with velocities above a certain limit, say, the line *AB* at 950 *m.*, increases very much with increasing temperature. This explains the rapid increase of vapor pressure, for, if the number of molecules continuously flowing into the liquid state increases, the density of the vapor, and thus its pressure, also increases until the number of condensing molecules, which has also increased due to the increase of density, is sufficient again to establish the dynamic equilibrium.

135. The Kinetic Calculation of the Vapor Pressure.—From kinetic considerations various authors (K Onnes, Dieterici, Jaeger, and others) have calculated the vapor pressure by methods which are not entirely similar but have the following general form:

From the liquid side $\frac{N_{liq}}{2}\bar{V}_x$ molecules strike a unit surface area in unit time (see **48**) when $\bar{V}_x$ is the average velocity component perpendicular to the surface and N_{liq} is the number of liquid molecules per cubic centimeter. The factor $\frac{1}{2}$ occurs because only one-half of all the molecules have a velocity component directed towards the surface. According to the statements in the preceding paragraph, however, it is not permissible to use the conception of an average velocity component in this case, but the distribution of velocities must be considered according to Maxwell's law in the form of Eq (69*a*) The number of molecules in the velocity interval between V_x and $V_x + dV_x$ is thus

$$dN_{V_x} = \frac{N_{liq}}{2}\sqrt{\frac{M}{2\pi RT}}\,e^{-\frac{MV_x^2}{2RT}}\,dV_x$$

The number of molecules within this velocity interval which strike the surface in unit time is

$$dN'_{liq} = V_x\frac{N_{liq}}{2}\sqrt{\frac{M}{2\pi RT}}\,e^{-\frac{MV_x^2}{2RT}}\,dV_x. \tag{134}$$

Now, all molecules having a velocity less than a certain limiting value V_l will be compelled to turn back by the attractive force of the other liquid molecules. In determining the total number N' of molecules which pass out from the surface, we are only concerned with those molecules which have a velocity greater than V_l or, in other words, Eq. (134) is to be integrated between $V_x = V_l$ and $V_x = V_\infty$ and thus the result is

$$N'_{liq} = \frac{N_{liq}}{2}\int_{V_l}^{\infty}\sqrt{\frac{M}{2\pi RT}}\,e^{-\frac{MV_x^2}{2RT}}\,V_x\,dV_x.$$

The integration can easily be performed by substituting $\frac{MV_x^2}{2RT} = y$, obtaining

$$N'_{liq} = \frac{N_{liq}}{2} B e^{-\frac{MV_l^2}{2RT}},$$

if the terms independent of V_l are combined in the constant B. The expression $\frac{MV_l^2}{2}$ represents the kinetic energy of one mole of molecules moving with the limiting velocity V_l and which are just able to get into the gas sphere According to the principle of conservation of energy, this amount of energy must be equal to the work performed against the attractive forces in checking or "braking" the molecule, *i e.*, it is equal to the work of vaporization At low temperatures the work of vaporization can be put equal to the heat of vaporization Λ_0, which gives

$$\frac{MV_l^2}{2} = \Lambda_0$$

and, therefore,

$$N'_{liq} = \frac{N_{liq}}{2} B e^{-\frac{\Lambda_0}{RT}}. \tag{135}$$

The number of N'_{gas} of molecules striking a unit surface area in unit time from the gas side is calculated in an exactly analogous manner, only all the molecules, even the slowest, pass the liquid surface. The integration must thus extend from 0 to ∞, the integral becomes equal to B since $\int_0^\infty e^{-y}dy = 1$, and the constant terms are the same Therefore,

$$N'_{gas} = \frac{N_{gas}}{2} B, \tag{136}$$

in which N_{gas} is the number of gas molecules per cubic centimeter The condition of dynamic equilibrium demands that $N'_{gas} = N'_{liq}$ and hence

$$N_{gas} = N_{liq} e^{-\frac{\Lambda_0}{RT}}.$$

While N_{liq} changes very little with temperature, the gas law must be applied to N_{gas}, giving $N_{gas} = \mathbf{N}\frac{p}{RT} = \frac{p}{kT}$, so that for the vapor pressure follows:

$$p = N_{liq} kT e^{-\frac{\Lambda_0}{RT}}, \tag{137}$$

or, in another form,

$$\ln p = -\frac{\Lambda_0}{RT} + \ln T + Const., \tag{137a}$$

an equation which at low temperatures is identical in principle with Eq. (131*e*). That Eq. (137*a*) does not completely agree with Eq. (131*e*) is mainly because the heat of vaporization was put directly equal to the work of evaporation and was assumed to be independent of the temperature. O Stern[1] succeeded in finding a kinetic derivation of a vapor-pressure formula

[1] *Z. Elektrochem.*, **25**, 66 (1919); see also SCHAEFER, CL., *Theoret. Physik.*, **1**, p. 539.

which may be connected with the thermodynamic formula at higher temperatures also and thus leads to an absolute calculation of the chemical constant *i*.

136. The Process of Fusion.—It has already been mentioned that the kinetic difference between the solid, crystalline phase and the liquid phase is due to the atoms or molecules of the solid substance being bound to definite positions of rest, while in the liquid they are more or less freely movable.

The transition from solid to liquid has been imagined as follows: Below the melting point the atoms vibrate about their positions of rest without strongly affecting each other; if the temperature is raised, the amplitude of vibration increases. By this means individual atoms approach each other and influence each other so strongly that they no longer return to their original positions. This phenomenon also may be used to explain the diffusion phenomena in solid solutions which are frequently observed just below the melting point. If the temperature is still further increased, the number of molecules which have been deflected from their paths of vibration increases rapidly, until, finally, at a definite temperature so few atoms return to their original positions that the whole structure of the crystal breaks down, or, in the usual terms, the crystal melts.

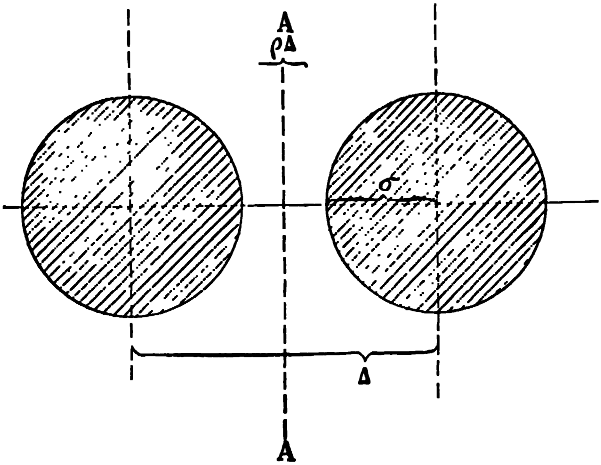

FIG. 33

F. A. Lindemann assumes that the atoms can deflect each other only when they touch during their vibrations, and, further, that the ratio of the atomic radius σ to the mean atomic distance Δ is constant (Fig. 33). With these assumptions it is possible to obtain a relatively simple and generally applicable relation between the characteristic frequency of the atoms, the melting point, and the atomic volume, even though it is only approximately correct.

Obviously, the atoms can swing out to the limit AA without being much disturbed, their amplitude thus represents a definite fraction of $\frac{\Delta}{2}$, which may be put equal to $\frac{\rho\Delta}{2}$. From Eq. (92) the vibrational energy of the atoms at this amplitude is

$$U_{mp} = \int_0^{\frac{\rho\Delta}{2}} bx\,dx = \frac{b\rho^2\Delta^2}{8}, \tag{92a}$$

if it is also assumed that the simple law of linear forces (Eq. (29)) is applicable. This amounts to stating that the atoms perform harmonic vibrations of the frequency (see also Eq. (31))

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{b}{m}}$$

For higher temperatures the Dulong and Petit law (Eq. (97a)) is sufficiently accurate and, therefore,

$$U_{mp} \sim T_{mp}$$

and, finally, as the result of Eq. (117),

$$\Delta^3 N = v_m,$$

if it is first assumed that (in all monoatomic substances) all the atoms are equal and are located in cubes.[1]

By combining the four previous equations the following equation is obtained

$$\nu_0 = Const\sqrt{\frac{T_{mp}}{M\,v_m^{2/3}}} \tag{138}$$

The term "*Const*," in which all the constants are gathered together, must be determined empirically, since it contains the unknown fraction ρ. The "*Const*" is about 2.8×10^{12} if ν_0 is stated in reciprocal seconds. A number of results obtained from this formula have already been given in Table 9, from which its applicability and the approximate correctness of its fundamental conceptions may be seen.

E. Grüneisen[2] has shown that these conceptions of the fusion process are in good agreement with the empirical facts mentioned in **62**, that simple solid substances expand a constant fraction (about 7.5 per cent) of their volume between absolute zero and their melting points.

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[1] In the considerations in **261**, which involve Lindemann's conception of the melting point, this simplification is neglected.

[2] *Ann. Physik*, **39**, 296 (1912).

From the foregoing it follows that in many respects the melting point bears the same relation to the solid phase as the critical point to the liquid. *Therefore, at the melting point the various solid substances are in corresponding states.* A number of properties, but not all, of solid substances can better be compared with each other at the same reduced temperatures, *i e.*, at the same fraction of the absolute melting point. The simplest example of this is the case of volume expansion.

137. Velocity of Crystallization.—From the kinetic conception of the fusion process it is quite clear that it is not possible to heat a solid beyond its melting point. On the other hand, the supercooling of a liquid may be easily understood, since the formation of a crystal generally requires a certain arrangement and, above all, a definite adjustment[1] of the molecules with respect to each other, the lack of which is a characteristic of the liquid phase, and which cannot always be established at once. In general, a certain time elapses before the essential number of molecules come together into the correct positions by purely accidental influences. Only after the formation of a small elementary crystal or crystallization nucleus, which then exercises a certain directing force on the neighboring liquid molecules and forces them to join together, does the cystallization proceed smoothly.

For such substances as most pure metals and a number of salts (NaCl, etc.), the crystals of which are built up directly of atoms and not of molecules, this consideration proves to be either not at all correct or at most correct within very narrow limits. Crystallization in this case depends, at the most, only very slightly on the arrangement of the atoms, it being sufficient for them to join together in just the positions in which they happen to be. Therefore, in no case up to the present could supercooling be observed in *pure* substances, which in the above sense can be called monatomic.

d. Applications

138. The Production of Constant Temperatures.—In the laboratory the most important practical application of the transitions from one phase to another is the production of constant temperatures. A mixture of the solid and liquid phase may be used as a temperature bath; it is advantageous if the heat of fusion is high, since then the bath can absorb or give off large amounts of heat without changing its temperature. In this respect water with its abnormally high specific heat of fusion (79.67 *cal.* per gram) is especially useful. (The heat of fusion of Hg is only 2.3 *cal.* per gram and that of benzol 30 *cal.*) The process of vaporization may also be used to obtain constant temperature, but in this case care must be taken that the pressure under which the substance is boiling is kept exactly constant. The temperature of the boiling liquid may be varied within wide limits by controlling the pressure, which is not possible in baths of fused solids. The numerous technical applications of fusion and vaporization processes cannot be considered further at this point.

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[1] * It is obvious that the more complex or irregularly shaped the molecules of a given substance are the more difficult it is to effect this adjustment. Hence, the enormous supercooling which is possible in some organic liquids, complex silicates, etc.

7. SOLUTIONS[1]

a. EMPIRICAL FOUNDATIONS

*** 139. General and Definitions.**—Having completed our study of pure substances in the gaseous, liquid, and solid states of aggregation, we now proceed to a study of the behavior of *homogeneous molecular mixtures* of substances, or *solutions*, as they are more often called. An understanding of the laws governing solutions and the process of solution is of the utmost importance in chemistry, as intimate mixing is a prime prerequisite for the initiation and control of chemical reactions.

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[1] *Parts *a*, *b*, and *d* of this section as well as some of the paragraphs of Section C have been written by V. K. LaMer with the cooperation of E. R. Jette, and replace the author's treatment for the reasons discussed in the Translators' Preface.

Many of the fundamental ideas upon which the theory of solution as presented in the following pages, are based, may be found in the early writings of Van Laar (*Z. physik. Chem*, **15**, 457 (1894); Proc. Acad Sci. Amsterdam **9**, 55 (1906); "Sechs Vortrage uber das thermodynamische Potentiale," Braunschweig (1906), G. N. Lewis (*J. Am. Chem. Soc.* **30**, 675 (1908); and Washburn (*ibid*, **32**, 653 (1910)). The translators wish to acknowledge their indebtedness to these writers and particularly to Washburn's "Principles of Physical Chemistry," which has had a considerable influence upon the form in which some parts of the material of Chapter 7 is presented.

*It is well known that gases will mix in any proportion and, theoretically, it should therefore be possible to effect a molecular mixture of any given number of substances by vaporizing them at a sufficiently high temperature. Actually, this is rarely practicable, since a great many substances, like sugar, decompose before vaporizing, and it becomes necessary to resort to liquid or solid solvents to effect a solution at ordinary temperatures.

*Liquids, in contrast to gases, possess varied and specific properties of miscibility with other liquids or gases, and solids. Thus, water dissolves an exceedingly large quantity of gaseous hydrogen chloride, liquid alcohol, or solid potassium hydroxide, but very little or no nitrogen, benzene, or silver. Evidently, miscibility is neither an exclusive property of the component in excess, which is often called the **solvent** in a mixture, nor of the other component, which is often called the **solute.** Instead, miscibility in the most general case depends upon the reciprocal effects of the properties of all the components upon one another as well as upon the specific individual properties of each, *i e*, we must be prepared to deal with specific interactions in certain cases. The terms solvent and solute have, accordingly, no meaning except as a convenient means of distinguishing one component from the other.

*The composition of a solution may be expressed in a variety of ways, *e g.*, in terms of the weight, volume, or number of moles of one component dissolved in either the weight, volume, or number of moles of the other component or of the resulting solution.

*For certain theoretical purposes, however, the composition of a solution is most advantageously expressed in terms of the mole fraction, as this procedure leads directly to the most general laws of solution and oftentimes permits of a mathematical treatment when other modes of expression fail.[1]

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*[1] The concept of mole fraction was introduced by Willard Gibbs as early as 1876, but it has received wide usage only in recent years, due no doubt to the fact that physical chemists were for a long time imbued with the idea that a general theory of solutions could be accomplished by extending van't Hoff's laws of the infinitely dilute solution, in which concentration is stated in volume molar units, by the use of correction factors similar to those in van der Waals' equation (see pp. 129, 141).

*The **mole fraction** N is the number of moles of the component considered divided by the total number of moles present; thus:

$$N_1 = \frac{n_1}{n_1 + n_2 + \cdots n_n}; \quad N_2 = \frac{n_2}{n_1 + n_2 + \cdots n_n}, \text{ etc.,} \tag{139}$$

where $n_1, n_2 \ldots$ refers to the number of moles of the components in question. Since the sum of the individual mole fractions always totals unity, the remaining mole fraction N_n may always be ascertained, when all but one are known, by the relation

$$N_n = 1 - (N_1 + N_2 + \cdots N_{n-1}). \tag{139a}$$

*However, for dilute solutions, and, particularly, for binary aqueous solutions, where it is easy to distinguish between the solvent and the solute, it has become customary to express the composition in terms of moles per liter of solution (the **volume concentration or molarity**) or in moles per 1000 *g*. (55.55 moles) of water (the **molality**). In highly dilute solutions, molalities and molarities become identical, but at lesser dilutions it is necessary to know the density of the solution to convert one to the other.

***140. Colligative Properties of Solutions—Osmotic Pressure.**—If a solution, say, of cane sugar in water, is separated from the pure solvent, or a solution of lower concentration, by a semipermeable membrane which permits the solvent (water) to pass through freely in either direction but selectively prohibits the passage of solute molecules, it will be observed that pure solvent always flows from the less to the more concentrated solution, as indicated by the rise of liquid in the capillary tube (Fig. 34*a*). This flow of solvent is known as **osmosis.** It ceases when sufficient pressure is applied to the solution at the membrane interface either by the development of a hydrostatic pressure, by the rising column of liquid or by the use of a piston (Fig. 34*b*, page 211), due to the fact that the pressure increases the tendency of the solvent to escape and flow from the solution to the pure solvent. The excess pressure upon the solution, as compared to the pure solvent, which is necessary to produce a state of equilibrium so that solvent flows equally in both directions defines the **osmotic pressure** of the solution experimentally.

*The magnitude of the osmotic pressure is a property of the solution which depends upon its concentration and not at all upon the nature of the membrane so long as the latter meets the requirement of semipermeability, namely, by being completely permeable to the solvent and impermeable to the solute.

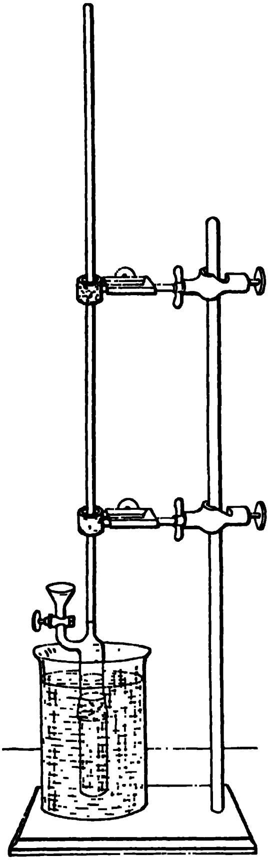

Fig 31*a*

*The phenomena of osmosis and the pressures developed from it play an exceedingly important part in many of the processes of life. It is found that the cell walls of many organisms (such as plant cells, blood corpuscles, bacterial cells, the intestinal wall, etc.) are almost completely impermeable to certain substances in aqueous solution which are toxic to them and more permeable to foodstuffs, like the sugars and amino acids. It is, of course, impossible to make absolute measurements of osmotic pressure with such cells, yet under the microscope the shrinkage or the swelling of a given type of cell can be followed, and by noting their behaviors in various solutions it is possible to determine at what concentrations the solutions possess the same osmotic pressure. Such solutions are called **isosmotic.** By knowing the osmotic pressure of one of the solutions in absolute units, it is possible to determine the others from the relative values obtained by the isosmotic method.

* Experimentally, it is very difficult to produce an ideal semipermeable membrane, but with some of the sugars—sucrose, glucose, and mannite—it has been possible to obtain direct, quantitative measurements by impregnating a cup of porous clay electrolytically with a membrane of copper ferrocyanide. The clay cup is necessary to aid the membrane to withstand the enormous pressures developed in concentrated solutions.

*In addition to osmotic pressure, it is well known that solutions show an elevation of the boiling point and a depression of the freezing point and vapor pressure over that of the pure solvent when a small amount of solute is used to produce the solution. All of these properties are related to one another thermodynamically, so that if the law governing one is known the others may be derived from it. Ostwald has called them the **colligative** (bound together) **properties of solutions.**

***140a. Direct Measurements of Osmotic Pressure.**—Quantitative measurements of osmotic pressure were first performed by the botanist Pfeffer (1877), but it has only been within recent years that Morse, the Earl of Berkeley, and their collaborators were able to surmount the great experimental difficulties and obtain a comprehensive series of measurements at various temperatures and concentrations for aqueous sugar solutions. Some of their more important results are contained in Table 26.

*From a consideration of Pfeffer's data, van't Hoff (1887) was able to enunciate the principle that the laws of osmotic pressure were analogous to the laws of perfect gases, since we get the *same numerical magnitude* for the osmotic pressure as though the solute itself existed as a gas in a space of the same volume as the solution and the gas pressure read directly, *i.e.*, the laws of ideal gases hold for the osmotic pressures (Π) or

$$\Pi = \frac{RT}{v_m} = \frac{n}{v} RT = cRT \quad \text{analogous to Eq. (73).} \qquad (140)$$

TABLE 26a.—OSMOTIC PRESSURE OF AQUEOUS CANE SUGAR SOLUTIONS (Atmospheres)

Volume	Weight	$T = 273°$			$T = 293°$			$T = 333°$		
Concentration, moles per liter, or 1000 g H_2O		π obs	π calc vol conc	π cal weight conc	π obs	π calc vol conc	π cal weight conc	π obs	π cal vol conc	π cal weight conc
0 098	0 1	2 40°	2 20	2 21	2 59°	2 36	2 41	2 72	2 68	2 73
0 1923	0 2	4 72	4 31	4 49	5 06	4 63	4 83	5 44	5 25	5 48
0 3701	0 4	9 44	8 30	8 97	10 14	8 90	9 64	10 87	10 11	10 93
0 533	0 6	14 38	12 00	13 50	15 39	12 8	14 5	16 54	14 65	16 48
0 6855	0 8	19 48	15 4	17 9	20 91	16 5	19 3	22 33	18 8	21 85
0 8273	1 0	24 83	18 6	22 41	26 64	19 9	24 1	28 37	22 7	27 35

*The data show that this is the case, within narrow limits of error, up to about 0.1 to 0.2 molar (volume concentration), but that at higher concentrations the observed pressure is greater than that calculated from Eq. (140). Morse, however, pointed out that, *if the results are expressed in terms of moles per 1000 g. of H_2O instead of liters of solution, better agreement was obtained at higher concentrations.* Some[1] consider this empirical change in units to be equivalent to a correction for the volume of the solute, just as the term $(v - b)$ in van der Waals' equation corrects for the volume of the gas molecules (*cf.* **143**).[2]

*On the basis of the validity of Eq. (140) and by deriving the thermodynamic relations connecting the various colligative properties, van't Hoff was able to develop a quantitative theory of solutions, but, unfortunately, it is restricted to the domain of dilute solutions[3] where Eq. (140) is valid.

*For this reason Eq. (140) will not be employed as the fundamental concentration law for the dissolved state in developing the laws of solutions, but more general, ideal laws valid for any concentration will first be developed, from which the van't Hoff laws may be derived as very important limiting cases.

*** 141. Effects of Environment. Perfect Solutions.** The discussion of the solid or gaseous state has shown how advantageous it is to define and study the laws relating to an ideal solid or gas before attempting to discuss the properties and laws relating to the more complex non-ideal state, even though the limiting states are not often met in practice. This procedure is all the more important in the study of solutions, for now there is a new variable to contend with: the composition of the solution. We shall, accordingly, be in a better position to answer the question as to what extent the behavior of a solution depends upon (1) its composition, and (2) the specific physical and chemical properties of its components, if we first study a group of solutions which are "ideal," *i.e.*, their properties follow some simple law of composition.

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[1] *Sackur, *Z. physik Chem*, **70,** 447 (1910); Porter, *Trans. Faraday Soc*, **13,** 123 (1919).

[2] *For the fusion of these viewpoints see Schay, *Z physik. Chem.*, **106,** 378 (1923).

[3] *Strictly speaking, it is valid only for the infinitely dilute solution.

*The simplest conceivable mixture would be that of two ideal gases (see **41**). If the gases chosen are not strictly ideal, they can be made to approximate ideality as closely as is desired by reducing the pressure upon them; *i.e.*, they are diluted with empty space until any mutual attractive or repulsive forces exerted upon the molecules by their neighbors are completely annulled. Under such conditions it is found that mixing is effected without absorption or evolution of heat and that the gas laws, $p_1v_1 = p_2v_2 = RT$, and Dalton's laws of partial pressures are obeyed by each gaseous component. *These laws are sufficient to define completely any perfect gaseous solution.* (Cf. **51, 88.**)

*It is more difficult to picture such a simple state of affairs for liquid mixtures; here the molecules of liquids lie close to one another and are therefore able to affect the behavior of their neighbors to a much greater extent than is true of gases. Thus, the two dissimilar liquids, benzene and mercury, will not mix to any detectable extent, while all gases mix freely. This fact can only be explained on the assumption that forces are exerted between the molecules of mercury which prevent their separation by the introduction of molecules of benezene, and *vice versa* On the other hand, there are many pairs of liquids, usually very similar to one another in their properties, which mix in all proportions, *e.g.*, the various hydrocarbons, water and alcohol.

*Since the proximity of the molecules of liquids precludes the ideal case of zero environmental effects such as exists in the perfect gas, we must be content to define **the perfect liquid solution** *as one in which a finite but constant environmental effect prevails throughout the entire range of composition.* This constancy of environment may be obtained in two ways; *viz.:*

1. By diluting the *solute* with such a large quantity of solvent that the *solute molecules* no longer exert any mutual attractive or repulsive forces upon neighboring *solute* molecules, and thus the constant environment of the *solvent* prevails; this is the basis of van't Hoff's theory of the infinitely dilute solution.

2. By choosing components possessing the same environmental properties, so that a molecule of either component will experience no change in the fields of force surrounding it when the composition is varied; *this is the basis of the perfect or ideal concentrated*

solution; to meet this requirement the components must mix in all proportions without thermal or volume changes.

*The dilution necessary to produce a constant environment in a liquid solution under (1) may be ascertained experimentally by a procedure similar to that for a non-ideal gas, namely, by determining that dilution or expansion beyond which further dilution or expansion fails to give a measurable thermal effect, *i.e.*, the heat of dilution has become zero. The total volume changes must also be zero on admixture. (Cf. **42, 51.**)

*Since (1) will not give a constant environment over the entire range of composition, it is evident that (2) is a more general procedure which will include (1) as a special case; further (2) does not require a distinction between the solute and solvent, so that the relations thus obtained must be valid for either component irrespective of whether one is in excess or not.

*But in order to employ (2), it is first necessary to establish a concentration law holding throughout the entire composition range for one of the colligative properties. Osmotic pressure could very well be chosen for this purpose, but its direct measurement involves serious experimental difficulties which has prevented its extension to substances meeting our requirements of a concentrated ideal solution; further, the kinetic interpretation of osmotic pressure is difficult for some persons to visualize and in concentrated solution is still a matter of dispute. On the other hand, many measurements have been made of the vapor pressure of concentrated solutions; this property is more amenable to a simple kinetic treatment, since the process is easy to conceive and the laws governing gases are better known and established than those of solids or liquids.

***142. The Molecular Lowering of the Vapor Pressure of a Solution. Raoult's Law.**—V. Babo (1848) and Wullner (1858) found empirically that the relative lowering of the vapor pressure of a solvent (p_0) by a non-volatile solute was independent of the temperature and proportional to the concentration of the solute.

*Raoult, from an exhaustive series of measurements published from 1878 to 1888, showed empirically that Wullner's law was most accurately represented when the concentration was expressed as the ratio of the number of moles of the non-volatile component

(n_1) to the total number of moles present, *i.e.*, proportional to the mole fraction or

$$\frac{p^0 - p}{p^0} = \frac{\Delta p}{p^0} = \frac{n_1}{n_1 + n_2} = N_1, \tag{141}$$

where n_2 is the number of moles of the volatile solvent of vapor pressure p^0.[1]

*That Raoult's law must result for a solution of constant environment may be shown as follows: given a mixture of two pure liquids X_1 and X_2 and changing the mole fraction of the first from N_1 to $N_1 + dN_1$ by the addition of a small amount of X_1, the vapor pressure p_1 of X_1 will change by an amount given by:

$$dp_1 = f(X_1, X_2)\, dN_1,$$

where $f(X_1, X_2)$ is some function depending upon the specific properties of X_1 and X_2 and their interactions towards one another. If the assumption is made that the physical and chemical natures of X_1 and X_2 are so nearly alike that the molecules of each are held under exactly similar constraints, it is apparent that the environmental forces acting upon a given molecule will not be affected by a change in composition, *i.e.*, $f(X_1, X_2)$ is constant for any value which may be assigned to N_1 or N_2, so that

$$dp_1 = k\, dN_1, \tag{142a}$$

where k is a constant measuring the environmental forces in the solution.

*Integration of Eq. (142*a*) yields

$$p_1 = kN_1 + Const.,$$

or the vapor pressure is a linear function of the composition. When $N_1 = 0$, we have no molecules of X_1, so that p_1 vanishes and the integration constant is zero. The meaning of k becomes clearer when we set $N_1 = 1$, then $k = p_1{}^0$, which is the vapor pressure of the pure component X_1, so that we have for the vapor-pressure law of a perfect solution that:

$$p_1 = p_1{}^0 N_1 \tag{142}$$

and, likewise, for the other component

$$p_2 = p_2{}^0 N_2. \tag{142b}$$

---

[1] *Raoult confirmed his law for fourteen solutes in ether He also pointed out that his law broke down in concentrated aqueous solutions.

Equations (142) and (142*b*) are often written as:

$$\ln p_1 = \ln p_1^0 + \ln X_1, \text{ or} \tag{142c}$$
$$d \ln p_1 = d \ln X_1, \text{ etc.} \tag{142d}$$

*Kinetically, Eq. (142) means that at equilibrium the number of molecules leaving a gas-liquid interface equals the number entering; this number will be directly proportional to the number of molecules of each species in the surface layer, since each species has an equal chance to escape into the vapor phase when the attractive and the repulsive forces between the different molecules are equal. This equality of forces also means that there will be no tendency to squeeze one species of liquid molecules into the surface layer from the interior of the liquid, at the expense of the other, so that Eq. (142) holds for the entire solution as well as for the surface layer. We are thus led to a conception of an escaping tendency characteristic of each particular molecular species. If the vapor follows the gas laws, this escaping tendency is accurately measured by the vapor pressure itself, but if the vapor does not follow the gas laws, the vapor pressure must be corrected for its deviations from the gas laws if it is to be used as a measure of the escaping tendency of X_1 in the solution. G. N. Lewis has called this "corrected vapor pressure" the **fugacity.**

*Fugacity thus becomes an exact measure of the tendency of a substance to escape from its surroundings as a perfect gas where the environmental effects are zero. For most purposes the vapor pressure serves as a sufficiently exact measure of escaping tendency and will be used as such henceforth in the discussion of ideal systems.

*Equation (142) is often called **Henry's law** from its discoverer, who found empirically that the solubility of a gas in a liquid—within limits if the solution is not strictly ideal—is directly proportional to the partial pressure of the gas. When p_1 refers to the partial pressure of gaseous X_1, then X_1 is nothing more than the solubility of X_1 in terms of mole fraction in the liquid X_2.

Since

$$\Delta p_1 = p_1^0 - p_1 \quad \text{or} \quad \frac{\Delta p_1}{p_1^0} = 1 - \frac{p_1}{p_1^0},$$

Eq. (142) may be transformed and

$$\frac{\Delta p_1}{p_1^0} = 1 - N_1 = N_2 = \frac{n_2}{n_1 + n_2}, \qquad (141)$$

obtained, which is **Raoult's law** when X_1 is considered volatile and X_2 non-volatile. *The laws of Raoult and Henry are thus different forms of the same law, depending upon whether the volatile component is considered as solvent or as solute*

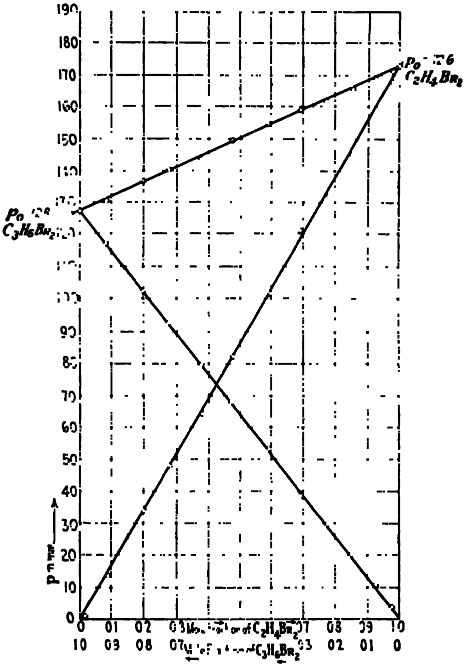

FIG. 35a

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*Equations (141) to (142*d*) have been accurately confirmed for a number of pairs of liquids, some of the more important examples are: (1) $C_2H_4Br_2 - C_3H_6Br_2$; (2) $C_6H_6 - C_6H_5Br$; (3) $C_6H_5CH_3 - C_6H_5C_2H_5$; (4) $C_6H_5CH_3 - C_6H_6$; (5) $CO_2 - CH_3Cl$; (6) $CH_3OH - C_2H_5OH$; (7) $CCl_4 - C_6H_6$. The vapor-pressure curves of the pair ethylene bromide-propylene bromide taken from Zawidski are given as an example in Fig. 35*a*. It will be noted that the liquids of each pair are either homologous or else resemble one another closely in chemical structure.

*An important corollary of Eq. (141) is that the components of a perfect solution must be miscible in all proportions. To prove this suppose either component saturates the solution forming two liquid layers. But at equilibrium the partial vapor pressure of a given component must be the same in both phases; since the partial vapor pressures are equal, the mole fractions, and therefore the two phases, must be identical.

* Equations (141) and (142) may also be stated in concentration units. Thus, in dilute solution n_1 may be neglected in the denominator of $N_1 = \frac{n_1}{n_1 + n_2}$, and if we multiply $\frac{n_1}{n_2}$ by the number of moles in a liter of solution or 1000 *g.* of the solvent, *i e.*, by $\frac{1000}{M}$, where M is the molecular weight of the solvent in the gaseous state, we have the desired result in terms of molarities or molalities respectively.

Thus Eq. (142) becomes

$$p_1 = p_1{}^0 \frac{n_1}{n_2} \cdot \frac{1000}{M} = k_{(\text{Henry})} \cdot c_1 \quad (\text{approx.}), \quad (142a)$$

which is the more usual form of Henry's law. Raoult's law likewise becomes:

$$\Delta p_2 = p_2{}^0 \cdot \frac{n_1}{n_2} \cdot \frac{1000}{M} = k_{(\text{Raoult})} \cdot c_1 \quad (\text{approx.}). \quad (141a)$$

b. THERMODYNAMIC RELATIONS

α. Perfect or Ideal Solutions

***143. Osmotic Pressure.**—The thermodynamic relation between osmotic pressure and the vapor pressure may be obtained by considering the enclosed system represented in Fig. 34*b*, where a solution A is separated from its pure solvent B by a membrane permeable to the solvent only. The pure solvent is under its own vapor pressure p and it is necessary to exert a total pressure P upon the solution in order to establish equilibrium and prevent the solvent from entering the solution. P is, obviously, equal to the osmotic pressure Π plus the vapor pressure, since Π is defined as the difference in pressures upon the two liquids. When equilibrium is established by means of the external pressure of the piston, p also becomes the vapor pressure of the solution. N is the mole fraction of the solvent.

*At equilibrium no work can be performed and, from **30**

$$d(A_{T,p}) \text{ (solution)} - d(A_{T,p}) \text{ (vapor)} = 0.$$

Also,

$$d(A_{T,p}) = -v\,dp \text{ from Eq. } (67d), \text{ (p. 62)},$$

where v refers to the volume occupied by one mole of substance and p to the pressure applied to that substance. If the molar

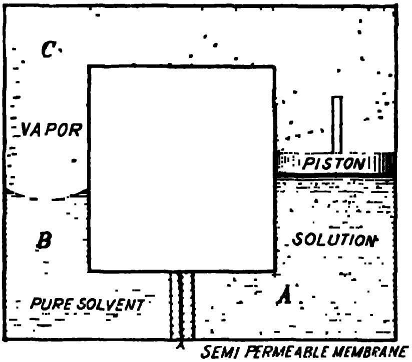

FIG. 31b

volume of the *vapor* is denoted by v_0 and that of the *pure solvent* by V_0, then:

$$-V_0 dP + v_0 dp = 0. \tag{143}$$

*Now an increase in P reduces the osmotic pressure between the solvent and solution, *i.e.*, the pressure of the piston acts in a direction opposite to the pressure of the solvent attempting to enter the solution, so that we may substitute $d\Pi = -dP$, whence it follows that

$$\left(\frac{d\Pi}{dp}\right)_T = \frac{-v_0}{V_0}. \tag{144}$$

*If the gas laws are now assumed for the vapor, $\frac{RT}{p}$ may be substituted for v_0 and then:

$$d\Pi = \frac{-RT}{V_0}\frac{dp}{p} = \frac{-RT}{V_0}\,d\ln p, \tag{144a}$$

or, introducing the vapor-pressure law (Eq. (142*d*), this becomes

$$d\Pi = \frac{-RT}{V_0}\, d\, ln\, N. \qquad (144b)$$

Integration of Eq. (144*a*) between the limits p and p_0 yields the expression

$$\Pi = \Pi - \Pi_0 = \frac{-RT}{V_0}\, ln\, \frac{p}{p^0} \qquad (144c)$$

and, likewise, integration of Eq. (144*b*) between the limits N and N_0 yields[1]

$$\Pi = \frac{-RT}{V_0}\, ln\, N, \qquad (145)$$

since $lnN_0 = 0$ and $\Pi_0 = 0$, the mole fraction of the pure component being unity.

*Equation (145) may be simplified by noting that $ln\, N = ln\,(1 - N_1)$ (Eq. (139*a*)) and expanding the latter in terms of a power series according to Eq (22*a*). Thus, in this case

$$\Pi = \frac{RT}{V_0}[-\,lnN] = \frac{RT}{V_0}[-\,ln\,(1 - N_1)]$$
$$= \frac{RT}{V_0}\left[N_1 + \frac{1}{2}N_1^2 + \frac{1}{3}N_1^3 + \quad . \quad\right] \qquad (145a)$$

N_1, however, refers to the solute and in dilute solution where n_1 is small $N_1 = \frac{n_1}{n}$ (approx.), which on neglecting higher powers of N_1 yields

$$\Pi = \frac{RT}{V_0}\frac{n_1}{n}. \qquad (145b)$$

But nV_0 = the volume of the *solvent* containing n_1 moles of solute, and thus Eq. (145*b*) is none other than Morse's modification of van't Hoff's law (see **140a**). In the highly dilute solution $\frac{n_1}{n} \cdot \frac{1}{V_0}$ also becomes equal to c the concentration of solute in *moles per liter of solution,* which yields the equation obtained originally by van't Hoff:

$$\Pi = cRT. \qquad (140)$$

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[1] *Strictly speaking, account should be taken of the fact that the molar volume V_0 varies, owing to the effect of the pressure P. This yields a correction term $-\frac{1}{2}\kappa P^2$ in Eqs (144*c*) and (145), but the compressibility κ of liquids is so small that no appreciable error is caused by its omission.

Since

$$\frac{n_1}{n} = \frac{\dfrac{n_1}{n_1 + n}}{\dfrac{n}{n_1 + n}} = \frac{N_1}{1 - N_1}$$

and

$$\frac{N_1}{1 - N_1} = N_1 + N_1^2 + N_1^3 + \quad . \; . \; .$$

Eq. (145b) also takes the form

$$\Pi = \frac{RT}{V_0}[N_1 + N_1^2 + N_1^3 + \; . \; . \; . \; (\text{approx.})]. \qquad (145c)$$

*On this view it is not surprising that Morse's modification more often fits the facts better than van't Hoff's equation, as the former is a closer approximation to the ideal equation, with which it differs only in higher powers of N_1.

*There are no direct measurements of the osmotic pressures of concentrated *ideal* solutions with which Eq. (145) may be tested directly, but Eq. (144c) may be tested by comparing the osmotic pressures calculated from the vapor pressures of Berkeley[1] (Table 26a, column 3) with the osmotic pressures observed by Frazer and Myrick[2] (column 2) which are found to be in excellent agreement. From its derivation Eq (145) must follow whenever Raoult's law holds.

TABLE 26b.—OSMOTIC PRESSURE OF CANE SUGAR AT 30°C

Conc. moles 1000 g. H_2O	Obs F. & M.	Calc. from vapor pressure, Eq (144c)	Calc from Eq (145b), Morse	Calc from Eq (145), ideal	Calc from Eq (140), van't Hoff
0 1	2 47	2 17	2 47	2 44	2 40
1 0	27 22	27 0	24 72	24 40	20 4
2 0	58 37	58 5	49 43	48 32	35 1
3 0	95 16	96 2	74 15	71 85	45 5
4	138 96	138 5	98 86	94 80	55 7
5	187 3	183 0	123 58	117 7	64 5
6	232 3	231 0	148 3	140 1	
6.5 (sat.)	252 8		173 0	151 2	

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[1] *BERKELEY, HARTLEY and BURTON, *Phil. Trans Roy Soc*, **218A**, 295 (1919).

[2] **J. Am. Chem. Soc.*, **38**, 1920 (1916).

*It will be noted that Eq. (145) (column 5) does not agree with the observed values in column 2, which can only be interpreted as indicating that *concentrated sucrose solutions are not ideal,*[1] as the thermodynamic derivation is completely verified using the vapor-pressure, Eq. (144c) above Scatchard[2] has advanced several lines of evidence which indicate that the cause of this non-ideality may be due to the formation of a comparatively stable hexahydrate of sucrose in solution. Column 6 shows that an error of 200 per cent is introduced if the volume concentration law of van't Hoff, which is valid only for infinitely dilute solutions, is used to calculate the osmotic pressure of a five-molar solution and that an error of 100 per cent would be introduced in using van't Hoff's law even if the solution were ideal!

***144. Boiling-point Law.**— Since the addition of solute always lowers the partial vapor pressure of the solvent, it is evident from Fig. 34c that the boiling point, which is represented by the intersection of the solution vapor-pressure curve and the ordinate for atmospheric pressure, will always be raised by the addition of a non-volatile component. If the added component is volatile, this may or may not result in an elevation of the boiling point, as the boiling point is the temperature at which the combined vapor pressures equal 760 *mm.* Hg.

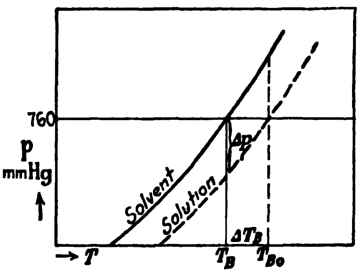

FIG 34c

*The thermodynamic expression for the elevation of the boiling point of a perfect solution formed by the addition of a non-volatile solute may be derived by setting the term $-d\ln p$ in the vapor-pressure law $-d\ln p = -d\ln N$ (Eq. (142*d*)), representing the *decrease* in vapor pressure due to a *decrease* in mole fraction of solvent, equal to the right-hand side of the Clapeyron-Clausius equation

$$d\ln p = \frac{\Lambda_v}{RT_B^2}\,dT_B, \qquad (146a)$$

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[1] *This is also shown by the vapor-pressure measurements and by freezing-point measurements, using Eq (145*d*), p 247.

[2] **J. Am. Chem. Soc.*, **43**, 2387, 2406 (1921).

representing the *increase* in vapor pressure with temperature which is necessary to compensate the effect of the solute. Here T_B is the boiling point and Λ_v is the latent of vaporization of the pure solvent.

*This gives

$$d\,lnN = \frac{-\Lambda_v}{RT^2_B}dT_B. \tag{146b}$$

*The boiling point $T_B = T_{B0} + \Delta T_B$, where T_{B0} is the boiling point of the pure component, so that $dT_B = d(\Delta T_B)$, which, on substituting in Eq. (146*b*) and integrating on the assumption that Λ_v is constant over this range of temperature, yields:

$$\Delta T_B = \frac{-RT_{B0}\cdot T_B}{\Lambda_v}\, lnN. \tag{146}$$

*This equation, which may be called the **general boiling-point law,** was carefully tested by Washburn and Read,[1] who found it to hold very accurately over a wide range for naphthalene and for diphenyl when dissolved in benzene

*If we confine ourselves to reasonably dilute solutions, Eq. (146), may be simplified in a manner exactly similar to that used for the osmotic pressure equation; namely, by expanding the logarithm in terms of the solute concentration $(1 - N_1)$, neglecting higher powers of N_1, noting that $T_B\cdot T_{B_0} \simeq T^2_{B_0} \simeq T_B^2$ and $\frac{n_1}{n_1 + n} \simeq \frac{n_1}{n}$, with the result that we get

$$\Delta T_B = \frac{+RT_B^2}{\Lambda_v}\cdot\frac{n_1}{n}. \tag{146c}$$

Letting c_1 equal the number of moles of X_1 in 1000 *g*. of X, then:

$$\frac{n_1}{n} = \frac{c_1 M}{1000}$$

or

$$\Delta T_B = \frac{M}{1000}\,\frac{RT_B^2}{\Lambda_v}\cdot c_1. \tag{146d}$$

where the constant term $k_B = \frac{M}{1000}\cdot\frac{RT_B^2}{\Lambda_v}$ is known as *molal*

---

[1] **J. Am. Chem. Soc*, **41**, 731 (1919) Consult for the accuracy of the approximate equations for molecular-weight determinations, and for the application of a very simple and accurate boiling-point apparatus devised by Cottrell, *ibid*, p. 721.

boiling-point constant and has the value +0.515° for water; an equation which is often used to determine the molecular weight of the solute X_1. (Cf. **158.**)

***145. The Freezing-point Law and the Solubility of Solids.**—The expression for the solubility of a solid X_2 in a liquid X_1, with which it forms a perfect solution, may be derived by first assuming that the solid has been melted and allowed to cool to T without solidification. This supercooled liquid form of X_2 will now mix with X_1 in all proportions, yielding the vapor-pressure line p_2 (Fig. 34d), as required by Eq. (140). However, the solution will be supersaturated with respect to the solid form of X_2 at higher concentrations, as the more stable form (solid X_2) always has a lower vapor pressure than the unstable form (supercooled X_2), and the solid form will separate on seeding with a crystal of X_2 until the partial vapor pressure of X_2 in the solution becomes equal to the vapor pressure of solid X_2 (p_2^s). The mole fraction of X_2 saturating the solution then becomes equal to N_2', which is given by the ratio

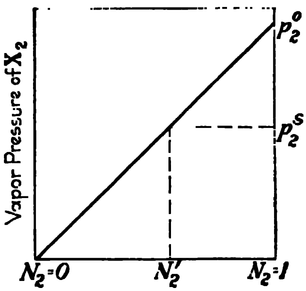

Fig 34d

$$N_2' = \frac{p_2^s}{p_2^0} \quad \text{or} \quad \ln N_2' = \ln p_2^s - \ln p_2^0$$

*This ratio may be calculated by subtracting the simple form of the Clapeyron-Clausius expression (Eq. (131a)) for the latent heat of sublimation from the similar expression for the latent heat of vaporization, yielding

$$\frac{d\ln p_2^s - d\ln p_2^0}{dT} = \frac{\Lambda_s - \Lambda_v}{RT^2} = \frac{\Lambda_f}{RT^2}$$

or

$$\frac{d\ln N_2'}{dT} = \frac{\Lambda_f}{RT^2}, \tag{147a}$$

where $+\Lambda_f$ is, obviously, *the latent heat of fusion* of the solid X_2, which, it is seen, *equals the latent heat of solution when Raoult's law is obeyed.*

*If we integrate Eq. (147a) between the limits T_M, the temperature of equilibrium between solid X_2 and the *solution,* and the melting point of the pure solid T_{M_0}, on the assumption that λ_f remains constant over this interval, we obtain the general solubility equation for a solid, which takes the form of Eq. (131*d*) when we introduce the value $R = 1.985$ *cal.* and convert to common logarithms:[1]

$$\log N_2' = \frac{-\lambda_f}{2.303R}\left(\frac{T_{Mo} - T_M}{T_{Mo} \cdot T_M}\right) = \frac{+\lambda_f}{4.57}\left(\frac{T_M - T_{Mo}}{T_M \cdot T_{Mo}}\right) \quad (147)$$

*Several general rules of solubility follow immediately from Eq. (147):

1. The solubility of a solid in an ideal solution is always greater the higher the temperature.

2. A solid having a higher melting point (T_{Mo}) is less soluble at a given temperature than another having a lower melting point (Lavoisier, 1793), unless the latent heats of fusion are much different. In spite of the fact that some of the examples given in Table 26*c* depart appreciably from the laws of perfect solutions, yet it can be seen that rule 2 holds very well

TABLE 26*c*

Solute	T_{Mo}	Solubility mol fraction at 25°C[1]	
		Benzene	Ideal
Anthraquinone	282°	0.0013	0.0023
Anthracene	217°	0.0081	0.0107
Phenanthrene	100°	0.207	0.221
p-dibrombenzene	87°	0.217	0.248
Naphthalene	80°	0.290	0.311

[1] Taken from HILDEBRAND, *J Am Chem Soc*, **39**, 2298 (1917)

3. The lower the heat of fusion the greater will be the solubility of the solid, other factors such as T_{Mo} and T_M being equal.

*When λ_f varies with the temperature, and particularly when the interval $T_{Mo} - T_M$ is large, an equation of the type of Eq. (132*a*) should be used in deriving Eq. (147), such as

$$\lambda_f = \lambda''_{f0} + (C_{p(\text{liq})} - C_{p(\text{solid})})T,$$

---

*[1] Equation (147) was first derived and tested by SCHROEDER. *Z. physik. chem.*, **11**, 449 (1893).

where Λ''_{f0} is not the true heat of fusion at absolute zero but an extrapolated value based on the specific-heat curves valid at higher temperatures[1] (*cf.* **131**), *i.e.*,

$$\Lambda''_{f0} = \Lambda'_{f0} - 4.571C''T,$$

which yields on integrating similar to the above:

$$\log N_2' = \frac{+\Lambda''_{f0}}{4.57}\left(\frac{T_M - T_{Mo}}{T_{Mo} \cdot T_M}\right) + \frac{(C'_{p(liq)} - C_{p\,(solid)})}{1.985} \log \frac{T_M}{T_{Mo}} \qquad (147b)$$

*According to Hildebrand,[2] we have the following data for naphthalene: $\Lambda_f = 4440$ *cal.*; $C'_{p(liq)} = 56.6 \frac{cal.}{deg.}$; $C'_{p(solid)} = 51.8 \frac{cal.}{deg.}$ (extrapolated to 353° *abs.*, the melting point of napthalene, from which we find Λ''_{f0} to be 2745 *cal*).

*Calculation according to Eq. (147) gives $N_2' = 0.323$, while Eq. (147*b*) gives $N_2' = 0.311$. The observed solubility in benzene is 0.290, which shows that a solution of naphthalene in benzene is almost ideal.

*By rearranging and substituting $-\Delta T_2$ for $T_M - T_{Mo}$ in Eq. (147), we get the **general freezing-point law**

$$-\Delta T_2 = \frac{RT_M \cdot T_{Mo}}{\Lambda_f} \ln N_2'. \qquad (148)$$

Here $-\Delta T_2$ represents the depression in the freezing point of the pure substance on the addition of X_1, since the temperature of saturation is none other than the freezing point of the solution separating X_2 as a pure solid. Inasmuch as Eq. (148) can also be written for $-\Delta T_1$, the depression of the freezing point of X_1 by the addition of X_2, it is evident that a binary system must have at least two freezing-point curves, as indicated by the graphs of Eq. (148) in Fig. 34*e*.

*The curve marked X_1 indicates that the solution is in equilibrium with solid X_1, and therefore may be designated either as the solubility curve of X_1 in a solution of X_1 and X_2, or as the curve representing the freezing-point depression of X_1 by addition of X_2. Likewise, the curve X_2 is the freezing-point or solubility curve of X_2. From this it is seen that in a general treatment of solutions, the solubility of the solid phase of the so-called solvent, which need not necessarily be in excess, is as much a colligative property of the solution as is its boiling point elevation or its vapor pressure. In using Eqs. (147) and (148), care must be taken that λ_f refers to the latent heat of fusion of the component separating out. The intersection of the two curves is called the *eutectic*[1]; it marks the separation of both components as a conglomerate.

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[1] *Of course, if the specific-heat curves are known down to the absolute zero, then Λ'_{f0} may be used instead.

[2] * Monograph on "Solubility," *A. C. S. Series*, p. 37, Chemical Catalog Co. (1924), original data by BOGOJAWLENSKI, *Chem. Zentr.*, (5), **9**, 945 (1905).

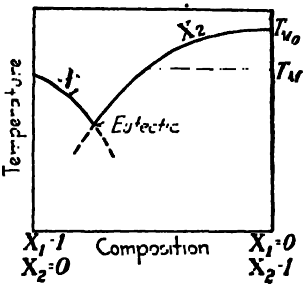

FIG. 34c

(β) Non-ideal Solutions

* **146. General.**—The development of the preceding sections was based upon the assumption that the components of the solution were so nearly alike *in the liquid state* that the fields of force[2] surrounding each molecule were the same; as a result, no change in environment occurs when the composition is varied.

*Now, if the fields of force surrounding the molecules of X_1 and X_2 are symmetrical, *i.e.*, *non-polar*, but one species X_2 has greater symmetrical fields of force, it would be expected that X_2 will associate itself more than X_1 and, consequently, tend to squeeze the molecules of X_1 out of solution. Raoult's law can no longer hold for the escaping tendency of X_1 and we find $p_1 > p_1^0 X_1$; *i.e.*, positive deviations from Raoult's law occur.

*Liquids which are non-polar are often called "normal," since they conform for the most part to the Eotvos surface-tension rule (see **102**), have low dielectric constants, and show normal entropies of vaporization (Eq. (131*h*)). Opposed to them are a group of polar or "abnormal" liquids distinguished by their higher dielectric constants and entropies of vaporization, and lower surface energies. This group includes water, liquid ammonia, the alcohols, amines, acids, and fused salts. They are much better solvents for electrolytes than the normal liquids and their solutions often show a considerable increase in conductivity over that of the pure components. The high dielectric constant indicates that there is an unsymmetrical distribution of the electrical charges in the molecules and the dielectric constant may be taken as one of the best measures of such polarity.

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[1] *PROF. JOHN JOHNSTON and his coworkers (personal communication) have recently shown that the various o-, m-, and p- nitroanilines form ideal mixtures and that by the use of an equation like 147*b* not only binary but ternary eutectics may be calculated with considerable accuracy.

[2] *The conception of a molecule or atom as the origin of an electrical field of force is developed in Sec. D and, for the present purpose particularly, in Part 4.

*Now this lack of symmetry in the distribution of the electric charges within the molecules leads to a specific or more directed attraction between the oppositely charged portions of these molecules and may be considered to be the reason for the much higher latent heats of vaporization, and internal pressures of polar substances, as well as their tendency to polymerize and form compounds with the other components in the solution.

*Thus, if the forces surrounding X_1 and X_2 are not symmetrical, they may have specific attractions for each other which are greater than those of the attractions of X_1 and X_2 for themselves. As a result, negative deviations from Raoult's law are to be expected, as each species will reduce the escaping tendency of the other species by combining with it to a greater or less extent, forming chemical compounds of varying stability, thus $p_1 < p_1^0X_1$, or $p_2 < p_2^0X_2$.

*The further elucidation of the causes of these deviations and their correlation with other physical properties of the pure components constitutes the most important phase in the present-day study of solutions. A complete understanding would permit the prediction of the solubilities and related colligative properties of a non-ideal solution of a given composition simply from a knowledge of the properties of the pure components. Needless to say, this has not yet been realized, for it must await a better understanding of the question of the gradation between electrostatic complexes and true chemical compounds particularly as regards the forces of cohesion and repulsion between atoms and molecules, and of valence in polar and non-polar compounds, with which it goes hand in hand (*cf.* **349** and **352**). We are thus restricted at the outset to simply pointing out certain general laws relating to these deviations and to the development of the effect of these deviations on the related properties.

*Figure 35*b* shows the vapor-pressure curves for a substance having either a positive deviation (curve *B*) or a negative deviation (curve *C*), from Raoult's law (curve *A*). If the positive deviation is very marked, as in curve *D*, the vapor pressure may exceed that of the pure liquid p_2^0, which, of course, is thermodynamically impossible (dotted portion), with the result that a

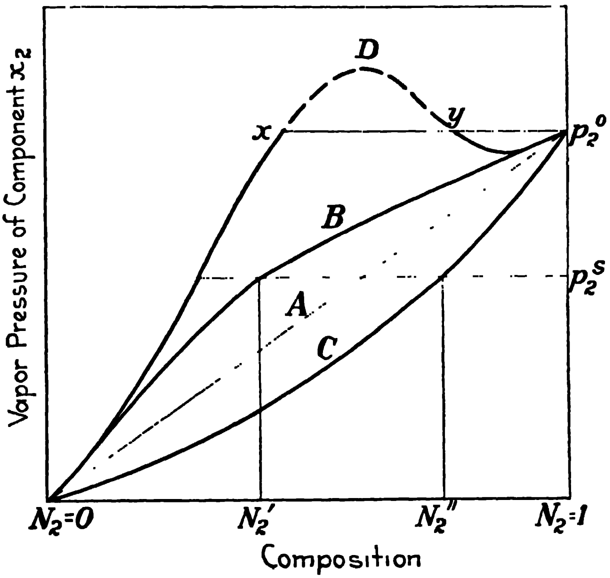

FIG. 35*b*.

state of incomplete miscibility and a separation into two layers occur, as indicated by the flat portion of *D* lying between *x* and *y*. The figure also shows (*cf*. Fig. 34*d*) that, if the component X_2 is a solid or gas and it exhibits a positive deviation, then the solubility of the solid or gas represented by N_2' will be less than for the ideal case, while a negative deviation will correspond to a solubility of N_2'' which is greater than the ideal solubility.

***147. Internal Pressure and Raoult's Law. The Solubility Gases in Liquids.**—Hildebrand has shown that the squeezing-out tendency referred to above is closely correlated with the difference in internal pressures of X_1 and X_2 *when both components are* *non-polar.* To test this hypothesis, he has calculated the internal pressures from the values of a and b in van der Waals' equation, surface-tension data, heats of vaporization, and, finally, from the coefficients of expansion and compressibility from which the internal pressure is obtained by the thermodynamic relation

$$\Pi_i = -T\frac{\left(\frac{\partial v}{\partial T}\right)_P}{\left(\frac{\partial v}{\partial P}\right)_T} \quad (cf.\ \mathbf{106}\ \text{and}\ \mathbf{107}).$$

*As the results thus obtained often vary in absolute magnitude, according to the method employed, he proposes the use of a

TABLE 26d.—RELATIVE INTERNAL PRESSURES REFERRED TO NAPHTHALENE

Substance		Substance	
Hexane	0 56 (56)	Trinitrophenol	1 14
Ethyl ether..	0 66 (62)	Dinitrophenol	1 15
Acetic anhydride	0 76	p-nitrophenol	1 17
Ethyl acetate	0 83	Anthraquinone	1 22
Carbon tetrachloride	0 84 (81)	Antimony trichloride	1 23
Bromobenzene.	0 94 (96)	Antimony tribromide	1 25
Benzene	0 94 (96)	Acetophenone	1 30
Toluene. ...	0 93 (84)	Aluminum bromide	1 30
Ethylene dibromide	0 95 (1 13)	Acetone	1 32
p-dibromobenzene	0 95 (1 09)	Napthylamines	1 33
Chloroform.....	0 95 (90)	Toluidines.	1 35
Chlorobenzene.. .	0 98 (96)	Benzoic acid .	1 38
NAPTHALENE...	1 00	Napthols. .	1 40
Diphenylamine	1 00	Trichloroacetic acid	1 42
Phenanthrene .	1 02	Aniline	1 46
Fluorene .	1 04	Sulfur. ...	1 70
Anthracene	1 05	Iodine	1 85 (1 82)
Diphenylmethane	1 06	Acetic acid	1 95
Triphenylmethane	1 07	Acetanilide	2 78
Nitrobenzene ..	1 07	Ethyl alcohol	2 90
m-dinitrobenzene .	1 08	Hydroquinone	3 27
Other nitro compounds	1 08	Methyl alcohol	3 35
Other nitro halides	1 08	Urethane .	3 50
Pyridine..	1 10 (1 17)	Resorcinol .	3 55
Carbon disulfide	1 13 (1 18)	Water	4 60 (4 55)

The unbracketed values are calculated from solubility data and are taken from HILDEBRAND'S, "Solubility," p. 116. The bracketed values are the results of calculations by the present writer (V. K. L.) using the other methods.

series of relative internal pressures based on solubility studies, all having been referred to naphthalene as unity (Table 26*d*).

*The results of his investigation may be summarized in the following general rules:

1. The deviations from Raoult's law are negligible when the difference in internal pressure is less than 10 per cent.

2. When the difference is greater than 10 per cent the *positive* deviation from Raoult's law is no longer negligible and is proportional to this difference.

3. When one component is polar and the other non-polar, the system behaves essentially the same as (2), though it is often more difficult to predict the result quantitatively.

4. When both components are polar, there is imposed upon the internal-pressure factor the tendency for selective attraction which is usually so much greater than the other factors that very marked *negative* deviations, as a rule, prevail instead.

*TABLE 26e—SOLUBILITIES OF GASES IN MOLE PER CENT

The solvents are in the order of increasing relative internal pressure

Solvent	Dielec const	H_2 20°	N_2 20°	CO 20°	O_2 16 – 20°	CH_4 25°	Cl_2 0°	$COCl_2$ 24°	Rn 20°
Ideal $\left(\frac{1}{p_o}\right)$	1 0		0 10	0 11	0 16	0 32	27 3	55	6 92
Hexane	1 9					0 31	27 0[1]		7 95
Amylacetate	4 8	0 016	0 094	0 13					
M-xylene	2 3	0 040	0 061	0 089	0 093	0 26		53	5 85
Toluene	2 3	0 037	0 053	0 077	0 082	0 21		53	5 20
Acetone (polar)	22 0	0 021	0 042	0 065	0 068				1 85
Benzene	2 3	0 026	0 041	0 061	0 065	0 18			4 31
Ethyl alcohol	26 0	0 021	0 033	0 045		0 11			1 44
Methyl alcohol	31 0	0 015	0 022	0 030		0 074			
Carbon disulfide	2 6		0 013	0 020					5.56
Water	80 0	0 0015	0 0013	0 0019	0 0017	0 024	0 75		0 02

Taken from HILDEBRAND, "Solubility," p 131 and the article by N W TAYLOR and HILDEBRAND (*J Am Chem Soc*, **45**, 682 (1923)) where a detailed discussion is given

[1] Heptane used as solvent.

*In Table 26*e* the solubilities of the gases (H_2, N_2, CO_2, O_2, Rn) are given in a series of solvents arranged in the order of increasing internal pressure. The ideal gas solubility is calculated from the relation $N = \frac{p}{p^0}$, where p is 1 *atm.* and p^0 the extrapolated[1] vapor pressure of the pure liquid at $T = 20°C$.

* It will be seen that the regular decrease in solubility is broken only for polar substances, as indicated by the high dielectric constant. Hevesy's data for the solubility of actinon (An) or actinium emanation fall in the same series of solubility as radon (Rn) or radium emanation, for which carbon disulfide is the only solvent behaving contrary to the rules given above. Since these two gases are isotopes, it would be expected that their solubilities *in terms of mole fraction* should be the same.

*** 148. Internal Pressure and the Solubility of Solids in Liquids.** For purposes of graphic representation, it is expedient to recast equations based upon the Clapeyron-Clausius equation into differential form by noting that $\frac{1}{T^2}dT = -d\left(\frac{1}{T}\right)$. Thus the solubility equation for solids (Eq. (147)) takes the form

$$-d\ \log N_2' = \frac{+\Lambda_f}{4.57}\, d\left(\frac{1}{T_M}\right), \qquad (147c)$$

so that by plotting $-\log N_2'$ against $\frac{1}{T_M}$ we get a straight line having its origin at the melting point of the pure component ($\log N_2' = 0$) and a slope which, when multiplied by 4.57, equals the heat of fusion in calories if the substance is ideal. Figure 36*a* shows the solubility of naphthalene dissolved in various non-polar solvents and plotted in that manner. If the solution is non-ideal, the slope at any point multiplied by 4.57 gives the **differential or partial molal heat of solution** at that concentration. This is the heat developed when one mole of solute is dissolved in an extremely large mass of solution so that the composition of the solution is not affected, *i.e.*, it is

$$\left(\frac{\partial \Lambda_{\text{solution}}}{\partial n_2}\right)_{N_1 = \text{Const}}$$

*In the present case, differences in internal pressure are the only important disturbing factors and it is found that the differential heat of solution is practically constant for almost all values of N_2, as indicated by the linear character of the curves; thus the differential heat of solution becomes equal to the **integral heat of solution,** $\Lambda_{(\text{solution})}$, at any point, where the latter is simply the heat developed on mixing the pure components.

---

[1] * When T is above the critical temperature this is, of course, a fictitious value.

*Space does not permit a development of the important relations involving the partial molal heat of solution or the analogous relations involving the **partial molal volume** $\left(\frac{\partial v}{\partial n_2}\right)_{N_2 = \text{Const}}$ and the **partial molal affinities** (*chemical potentials*) $\left(-\frac{\partial A_{T,p}}{\partial n_2}\right)_{N_2 = \text{Const}}$

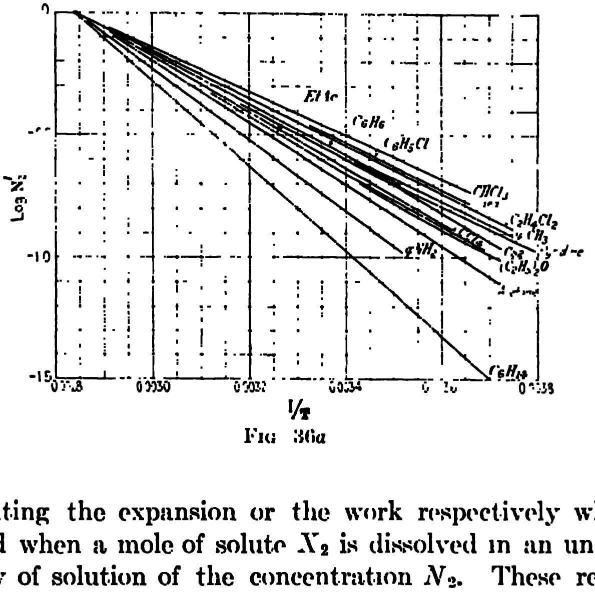

FIG 36a

representing the expansion or the work respectively which is obtained when a mole of solute X_2 is dissolved in an unlimited quantity of solution of the concentration N_2. These relations show that it is a necessary, but not always a sufficient, requirement for a perfect solution that the components mix in all proportions without change in either volume or temperature alone.

*Although a complete and *exact thermodynamic* treatment of solutions always necessitates the use of partial molal rather than integral properties, it is often possible to gain valuable information regarding the direction and the extent of the non-ideality of a solution directly from the thermal and volume changes which occur on mixing the pure liquid components. Thus, a positive deviation from Raoult's law is *generally* associated with an absorption of heat and an expansion in volume, while the converse is *usually* true for negative deviations. Details regarding the determination and use of the partial molal quantities in the treatment of solutions are to be found in the papers of Bronsted,[1] Lewis and Randall,[2] and in Hildebrand's monograph.[3]

*It will be noted from the relative position of the curves in Fig. 36*a* that the solubility of naphthalene decreases in the order: ideal solution, chlorbenzene, benzene, toluene, carbon tetrachloride, ethyl acetate, ether, and hexane, which is also the order of decreasing internal pressures (*cf.* Table 26*d*). Proceeding to solvents of internal pressure greater than naphthalene, the solubility again decreases in the order ethylene chloride, carbon disulfide, and aniline, as expected from rule 2. The abnormal solvent power of chloroform, which should be about that of benzene, is due no doubt to its slight polarity and the solvation resulting from this (*cf.* **191***a*).

*Mortimer[4] has shown that the equation

$$\log N_2' = \frac{f_s \ \Lambda_f}{4.57}\left[\frac{T_M - T_{M_0}}{T_M \cdot T_{M_0}}\right] \tag{149}$$

holds not only for non-polar substances as above, but often holds with considerable accuracy when one component is polar; $f_s \cdot \Lambda_f$ is obviously equal to the partial molal heat of solution of a saturated solution and f_s is a factor which depends only upon the differences in relative internal pressure, K_1 and K_2, as given in Table 26*d*.

*When

$$K_1 > K_2 > 1 \qquad f_s = K_1 - K_2 + 1$$

$$K_2 > K_1 < 1 \qquad f_s = \frac{1}{K_1} - \frac{1}{K_2} + 1$$

$$K_1 > 1 > K_2 \qquad f_s = K + \frac{1}{K_2} - 1.$$

*Some of Mortimer's results shown in Table 26*f* bear this out.

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[1] **Z. physik. Chem.*, **64**, 641 (1908), **68**, 693 (1910).

[2] **J. Am. Chem. Soc.*, **43**, 233 (1921)

[3] **Loc. cit.*, chap. 6.

[4] **J. Am. Chem. Soc.*, **44**, 1416 (1922), **45**, 633 (1923).

TABLE 26*f*.—SOLUBILITIES IN MOLE FRACTION AT 20°C.
Calculated by Eq. (149)

Solvent	Solute p-dibrombenzene		Fluorene	
	Obs	Calc	Obs	Calc
Ideal .		0.207		0.137
C_6H_6	0.202	0.202	0.105	0.109
$C_6H_5CH_3$	0.197	0.200		
CCl_4 .	0.159	0.163	0.078	0.084
$C_6H_5NO_2$ . .	0.144	0.163	0.118	0.126
$C_6H_5NH_2$	0.085	0.085	0.056	0.058
C_6H_5OH	0.017[1]	0.151		
C_2H_5OH	0.028[1]	0.008	0.005	0.003

[1] Polar solvents

* In fluorene it will be noticed that the closest approach to ideal solubility occurs with benzene and nitrobenzene, which also approach fluorene most closely in internal pressure.

* In Table 26*g* the latent heat of fusion has been calculated from the solubility in a substance of known relative internal pressure and the result compared with the value determined calorimetrically. With the exception of benzophenone, the agreement is excellent and confirms the theory, since the relative internal pressures used in the calculation were based on the solubility relations of naphthalene alone. The variations in the last column show how greatly these substances deviate from the simple relation (Eq. (126)), where, according to Walden,[1] the constant should equal approximately 13.5.

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[1] * *Z. Elektrochem.*, **14,** 713 (1908)

TABLE 26g.—LATENT HEATS OF FUSION OF ORGANIC SUBSTANCES CALCULATED FROM SOLUBILITY CURVES AND DIFFERENCES IN THE RELATIVE INTERNAL PRESSURES OF SOLUTE AND SOLVENT (EQ. (149))

Substance	T_{M_0}	λ calc.	λ obs	$\frac{\lambda_f}{T_{M_0}}$ (Eq (126))
	Hydrocarbons			
Benzene	278.5	2330	2350	8.36
p-xylene	287.4	3840	4170	13.4
Diphenyl	343.2	4390	4390	12.8
Anthracene	489.6	6870	6890	14.0
	Halides			
Ethylene dibromide	287.8	2540	2540	9.0
p-dibrombenzene	360.0	4850	4860	13.5
	Nitro compounds			
m-dinitrobenzene	363.0	4900	4870	13.5
	Amino compounds			
Aniline	267.5	1940	1940	7.26
Diphenylamine	325.7	4020	4050	12.3
	Oxygen compounds			
Phenol	313.6	2260	2340	7.2
Thymol	322.2	2970	2980	9.2
Benzophenone	388.0	3800	4310	11.8
Urethane	318.2	3630	3630	8.03

***149. Solutions of Polar Components.**[1]—Although in many cases it is possible to explain the behavior of a system in which one component is polar and the other component is non-polar on the basis of the differences in internal pressures alone, this explanation is not always successful in highly polar mixtures and breaks down completely when both components are polar. In this case the factor of selective attraction leading to compound formation between the components overshadows and obscures any effect which the differences in internal pressure may exert. Unfortunately, at the present time it is very difficult to predict in advance how great the tendency toward compound formation will be for a given set of components, as the latter depends not alone upon the relative polarities of the components, but also upon the specific character of the polarity. However, it is known in general that a substance which exhibits basic properties tends to combine with substances exhibiting acidic properties, and since acidity and basicity are only relative manifestations of a given type of polarity it is reasonable to expect that two acids may combine to form compounds when one is a weak and the other a much stronger acid. Thus, the weak acid phenol ($K_a = 10^{-10}$) gives little evidence of forming a compound with chloracetic acid ($K_a = 1.55 \times 10^{-3}$), but does form a definite equimolecular compound with the much stronger trichloracetic acid ($K_a = 2.57 \times 10^{-1}$).[1]

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[1] * In using the term compound formation as an explanation for the behavior of polar components, it should be kept clearly in mind that the weak unions referred to in this paragraph as compounds may often be of a quite different character from such typical chemical compounds as CO_2, H_2O, etc. There is a growing body of evidence resulting from recent studies of the physicists Debye, Born, Fajans and their collaborators that *in solution* solvates may be nothing other than a closer packing of the solvent molecules in the neighborhood of ions and even neutral molecules when the latter are polar, owing to the polarization which their electrical fields produce upon the surrounding solvent molecules. Any orientation of solvent molecules thus set up is being disturbed continually by the heat motion of the various particles and therefore the complex as a whole is of indefinite composition. Although these electrostatic complexes of indefinite composition are of prime

*The net effect of compound formation is to produce negative deviations from Raoult's law, which is manifested in weakly polar components by vapor-pressure curves which sag like curve C' in Fig. 35*b*. A mixture of acetone and chloroform gives a vapor-pressure curve of this nature, even though a definite compound cannot be isolated at ordinary temperatures. As the polarity increases, the sagging increases and, finally, in the limiting case where liquid X_1 and liquid X_2 have such a selective attraction for one another that they have united almost completely to form a stable compound, say, of the equimolecular type represented by the composition $X = 0.5$, we should find that the vapor pressures of X_1 and X_2 at this composition will

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importance in solution, nevertheless definite compounds may exist; for example, in cases where an equilibrium exists between the solution and a definite solid solvate. Consult FAJANS, "Die Naturwissenschaften," **9,** 729 (1921), **11,** 165 (1923) and **191***a* for a discussion of some of these points and for references to earlier work

[1] *KENDALL, *J. Am. Chem. Soc.*, **38,** 1309 (1916).

approach zero; the vapor-pressure curve of either component will be composed of two halves concave to the abscissa and which touch this axis at $N = 0.5$. Compounds are undoubtedly formed in solution in systems lying between this limiting case and that of the ideal solution, but they are usually so highly dissociated or difficult to isolate that they escape detection. Thus, solvates of the general type $(H_2O)_x \cdot (HCl)_y$ exist in a dilute aqueous solution of HCl just as the compound $NH_3 \cdot HCl$ exists when HCl is dissolved in liquid ammonia.

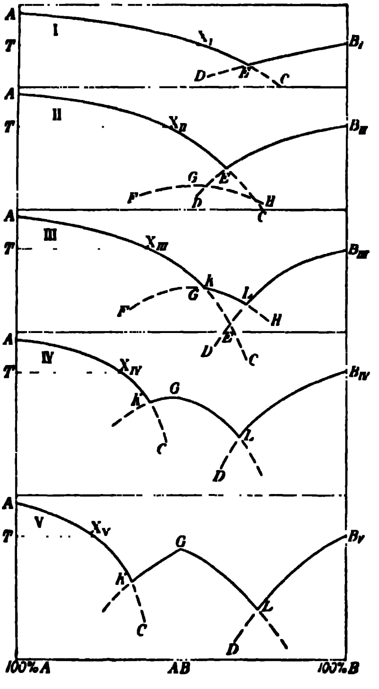

Fig 36b

*Systematic vapor-pressure measurements on systems showing graded polarities, and therefore graded tendencies toward compound formation, have not been carried out, owing, no doubt, to the difficulties involved in measuring the very minute partial vapor pressures of components in compounds. The effect of such deviations from Raoult's law may be studied more easily by means of the other colligative properties and it is found in such cases that the tendency to compound formation increases the solubility of X_1 if X_2 is considered the solvent, and also increases the freezing-point depression, boiling-point elevation, and osmotic pressure above the ideal.

*The effect of the increasing stability of a compound upon the freezing point and solubility is shown in Fig. 36*b*, summarized from the work of Kendall[1] and his co-workers.

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[1] *Kendall, Davidson, and Adler, *J Am. Chem Soc*, **43**, 1485 (1921), from whom we quote extensively Experimental data for these different types of curves are to be found in Kendall's earlier work, *ibid.*, **36**, 1722 (1914), **39**, 2303 (1917).

*To facilitate comparison of the curves, it is necessary to note that A represents the same temperature throughout the melting point of the pure substance A. B_I to B_V are different components possessing the same melting points, but exhibiting increasing tendencies toward compound formation. Curve I indicates the ideal system $A - B_I$, where compound formation is entirely absent. The solubility curve of A in B_I is that of Eq. (147). In curve II a compound is formed (line FGH), but is so highly dissociated that it never enters the stable region (*cf.* **162** (2)); in curve III compound formation is more extensive and the solubility curve of the compound AB_{III} possesses a limited stable interval KL; in curve IV the compound is stable at its melting point, *i.e.*, it possesses a maximum at G; finally, in curve V the compound AB_V is not dissociated at all into its components in solution, the system consisting of two simple systems of the type shown in curve I compressed into one composition range.

*The essential point to be noted in these systems is *the depression of the curve AC from its ideal position.* If only part of the total A exists uncombined in solution, then, since the solution will not become saturated with respect to A until the mole fraction of uncombined A reaches the ideal value, the total mole fraction of A in the saturated solution must exceed this ideal value by an amount depending upon the stability of AB in the liquid state. The solubility of A at any fixed temperature T consequently increases regularly as we pass from curve I to V, as is shown by the points X_I, X_{II} X_V, representing the composition of the saturated solutions at the temperature T. Although but one compound AB is considered in the above, in practice, numerous compounds may actually form in various stages of dissociation (*cf.* the $FeCl_3 - H_2O$ system (Fig. 41)), which, of course, makes the problem very complicated. In addition to compound formation, the association of the pure components as well as the internal-pressure factor must be accounted for also, so that at present it is very difficult to predict quantitatively the colligative properties of concentrated polar mixtures, and particularly those of aqueous solutions. However, the following table (26*h*) shows, in general, that the solubility increases with an increase in polar character measured by the strength of the acid solvent.

TABLE 26*h*

Solubility of dimethyl pyrone at 40°C. M.p. = 132.1°		Solubility of benzoic acid at 50°C. M.p. = 121°	
Solvent	Mole per cent solute in saturated solution	Solvent	Mole per cent solute in saturated solution
Acetic acid	40.2	Benzene. .	17.6
Formic acid	46.8	Acetic acid	27.7
Chloracetic acid	50.6	Chloracetic acid	30.2
Dichloracetic acid	53.5	Dichloracetic acid	42.5
Trichloracetic acid	54.3	Trichloracetic acid	49.5[1]
Ideal (calc.)	41.5		

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[1] It will be noted in Table 26*h* that the solubility of benzoic acid in the concentrated acids is counter to that predicted on the basis of the solubility product law (Eq. 206), which is valid only for dilute solutions.

*A similar though less marked effect is noted for the solubility of ice at −5°C. (m.p. 0°) in which the mole per cent of solute is 95.01 per cent for acetic acid, increasing in the order: *α* oxypropionic acid (95.49 per cent), d-tartaric acid (95.78 per cent), hydrochloric acid (96.19 per cent). The ideal solubility is 95.26 per cent.

*It can be shown (Kendall) that electrical conductivity also manifests itself parallel with the tendency of the solute to form compounds (solvates) with the solvent. Electrical conductivity, which is explained by the theory of electrolytic dissociation, must be reserved for a later section (**182** to **193**).

*It is sufficient at this point to state that the appearance of conductivity in mixtures whose pure components do not conduct the current appreciably, such as HCl and H_2O, indicates very marked deviation from ideality and, up to the present time at least, these deviations from the laws of perfect solutions have only been treated rigorously (see **191*a***) in solutions which are so dilute that it makes very little difference whether the concentration is expressed in terms either of mole fraction, molality, or molarity. In other words, it makes little difference in such dilute solutions whether the ideal law is considered to be the general logarithmic form (Eq. 145) or the more simple linear form (Eq.

140) used originally by van't Hoff, which closely approximates to the former up to about 0.1 molal, as shown in **143** and **144.** On the other hand, in considering concentrated solutions, appreciable errors will be introduced, in fact, quite erroneous deductions[1] have been drawn in the past regarding the nature of solutions by using the approximate equation instead of the general equation of a perfect solution involving the mole fraction as the norm of ideal behavior.

* Unfortunately, the mole fraction scale does not yield a simple theoretical relation between the concentration and the deviations from ideality, since these deviations depend upon the forces exerted between the individual molecules which in turn depend upon the distances between the molecules. It appears that the whole problem of concentrated solutions can be treated most simply by determining the deviations from ideality in terms of the mole fraction and then considering the functional relation of the deviations in terms of molarities,[2] because the distances between individual molecules have a more direct relation to the volume concentration.

* We may conclude our survey of the thermodynamic properties of solutions with the statement that the laws of perfect solutions hold with an accuracy of about 1 or 2 per cent for:

1. Non-polar substances of like internal pressures at any composition and to a less degree depending upon the internal pressure as described in **147** and **148.**

2. Weakly polar mixtures where the solute resembles the solvent in chemical nature, such as solutions of the sugars and alcohols in water up to a concentration of about $N = 0.05$, or 2 molar.

3. Aqueous solutions of most non-electrolytes to about $N = 0.01$, or 0.5 molar.

4. Aqueous solutions of strong uni-univalent electrolytes to less than 0.0001 molar owing to the marked effect of the polar electric charges. With higher-valence electrolytes the dilution

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[1] * A striking example is given by Washburn in his article "Hydrates in Aqueous Solution," *Mass. Inst. Tech. Quart*, **21**, 367 (1908).

[2] * The effect of the choice of the concentration scale on the form of certain of the thermodynamic deviation equations is discussed by Bjerrum (*Z. physik. Chem.*, **104**, 406 (1923)).

must be even higher than this if we are to expect the gas laws to hold within the limits set above. However, if other salts are present in constant amount and in quantities so large (2.0 M) that a variation in concentration of the salt present in small amount does not appreciably affect the total ionic concentration, it has been found[1] that the gas laws hold remarkably well even up to 0.2 molar. The presence of excess of foreign salts simply maintains a constant electrical environment (ionic strength), with the result that Raoult's law holds.

c. KINETIC THEORY

150. Osmotic Pressure as a Result of the Energy-distribution Law.—It has been shown empirically that the gas laws (Eq. (73)) hold for *dilute solutions* as well as for gases. The most important problem in the consideration of solutions from the kinetic viewpoint is to prove that this empirical result follows from the common origin of the phenomena in the two states.

If we consider the kinetic derivation of the gas law (see **48**), we must be convinced that it follows merely from a consistent application of the laws of classical mechanics which, especially for the molecular mechanics, culminate in the energy-distribution law. Furthermore, it was assumed that the gas molecules were freely movable, small in dimensions, and exercised no forces upon each other except during collision, but at no time was it necessary to estimate the length of the free path of the molecules, the form of path described by the gas particle, etc. Therefore, according to Dalton's law (see **41**), even the partial pressure of an individual gas in a gas mixture was not affected by increasing the number of collisions.

Altogether, four of the assumptions made for gases are directly applicable to dissolved particles: the applicability of the laws of mechanics (validity of the energy-distribution law), free mobility, small dimensions, and the absence of forces between the atoms. *It is, therefore, possible to apply the kinetic proof, given for the gas laws in* **48**, *directly to osmotic pressure.* As a matter of fact, the only real difference between gas molecules and dissolved molecules is the form of their paths of motion. Gas molecules describe a zigzag path with relatively long distances between the changes of direction, since they can collide only with similar particles. The dissolved particle, on the other hand, strikes the liquid (solvent) particle exceedingly often therefore it changes direction much oftener, and thus describes a zigzag path with very much shorter displacements. The form of the path of the individual molecule, of course, exerts a considerable influence on many phenomena, such as diffusion, but not on the origin of the thermal pressure. Therefore, neglecting the secondary conditions mentioned above, if the energy-distribution law is applicable to dissolved particles, it must necessarily follow that the gas law must be applicable. Conversely, the validity of the gas law for solutions signifies that the energy-distribution law prevails in this case as well as in gases.

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[1] *BRONSTED, "Applicability of the Gas Laws to Strong Electrolytes," *Kgl. Danske Videnskab. Selskab*, *Math.-fys. Medd.* (in English), **3**, 9 (1920); see also *Medd. Nobelinst.* (in English), **5**, No 25 (1919) and *Z. physik. Chem.*, **103**, 307 (1922).

In spite of the numerous earlier attempts, the kinetic significance of osmotic pressure with full emphasis on the simple and convincing relation between osmotic pressure and the energy-distribution law was first demonstrated by Einstein (1905).

151. The Flow of the Solvent into the Osmotic Cell. The Lowering of the Vapor Pressure.—The origin of the pressure exercised by dissolved particles upon a membrane which they cannot penetrate is not difficult to understand after what has already been said, although it does perhaps appear paradoxical at first that the solvent particles should flow through a fixed semipermeable partition into the cell against the osmotic pressure. In spite of this, the phenomenon is a simple mechanical result of osmotic pressure.

A dissolved particle, conceived as being in a state of very lively motion, strikes against the semipermeable wall, is thrown back from it, strikes one or more solvent particles in the next instant, and is thrown back towards the wall by them. The solvent molecules thus receive an impulse directed away from the wall which, on the whole, is just as great as the impulse towards the wall received by the dissolved particle. The process is illustrated diagrammatically in Fig. 37, in which the left half represents a dissolved particle (large circle) just striking the semipermeable wall and receiving an impulse back into the solution. The right half represents the same particle very shortly afterwards, when it has collided with solvent particles (small circles) and has been forced to turn back, the latter receiving impulse towards the interior of the solution. The solvent particles which have been struck transfer their impulse to their neighboring particles, so that finally the solvent flows slowly inwardly through the membrane which is permeable to it. Only when there is a force, such as hydrostatic pressure, which opposes this motion, is the inflow made slower and finally ceases entirely.[1]

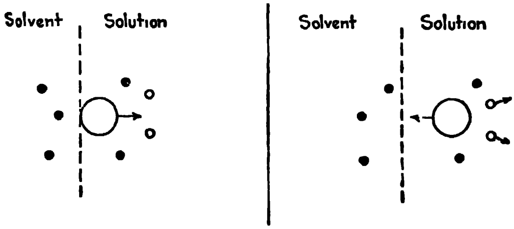

Fig. 37.

The surface between a solution and its vapor also acts as a semipermeable membrane. The solvent particles are able to pass through the surface, even though with considerable change of velocity, but the dissolved particles are bound to the liquid phase, provided, as has been assumed, the dissolved particles are non-volatile.

Just as at the semipermeable wall, the solvent molecules receive from the dissolved molecules an impulse towards the interior of the solution which acts in the same direction as the cohesion pressure. As a result of this increase in the cohesion pressure the solvent molecules are more firmly held in the liquid state than before, and *therefore the vapor pressure of the solution is smaller than that of the pure solvent.*

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[1] * For a derivation of Eq. (145) for the osmotic pressure of a perfect solution which is based upon the earlier kinetic considerations of van Laar, see WASHBURN (*J. Am. Chem. Soc.*, **32**, 657, 1910). By picturing the origin of the osmotic pressure of non-electrolytes as due to a difference in *solvent* pressure, SCHAY (*Z. physik. Chem.*, **106**, 378 (1923)) has shown that it is valid to consider the osmotic pressure to be numerically equal to the pressure of the solute particles only at infinite dilution. His analysis shows that, although at finite concentrations the partial pressure of the *solute* molecules is not equal to the osmotic pressure, the effective partial pressure of the solvent molecules is equal to the osmotic pressure, and his work may be taken as a confirmation of the views set forth in **151**. Recently, DEBYE (*Rec. trav. chim. des Pays Bas*, **42**, 597 (1923), see also **188c**) has developed a kinetic theory of the osmotic pressure of strong electrolytes which is in accord with the results of thermodynamic reasoning as well as experimental data for concentrations up to about 0.1 molar.

152. The Osmotic Pressure of Visible Particles.—While the applicability of the energy-distribution law, according to the behavior of solid substances, becomes increasingly doubtful as the mass of the particle becomes smaller and, therefore, as its vibration frequency increases, there is at present no basis for limiting the sphere of its application as far as relatively large and heavy particles are concerned. Relatively heavy particles must, therefore, also exercise an osmotic pressure which follows the gas laws, but, of course, the particles must move freely, their diameters must be small in comparison with the distances between them, and they must not mutually attract each other. These conditions are approximately fulfilled by very small liquid or solid bodies suspended in liquids (emulsions suspensions) and a certain class of colloidal sols (suspension colloids); therefore, the laws of osmotic pressure must also hold, even though the individual particles can be followed by means of the microscope or ultramicroscope.

Since the particles are quite large in comparison with molecules, only relatively few of them may be contained in a unit volume, *i.e.*, the molar concentration is always very small. For this reason the osmotic pressure is so small that the customary methods give at best very uncertain results. Other methods can be used, however, which, in turn, are not applicable to ordinary solutions.

An accurate knowledge of the osmotic pressure of colloidal sols with visible particles is of interest not only because the molecular weight M of the particles can then be calculated, according to the gas laws, but the size and mass m of the actual particles can also be determined to some degree of accuracy by several different methods. From these *it is possible to determine the Avogadro number* $\mathbf{N}$ *by means of the relation* $M = m\mathbf{N}$.

153. Sedimentation Equilibrium.—One of the most elegant methods for determining the Avogadro number, although it avoids an explicit calculation of the osmotic pressure itself, is based upon the measurement of the decrease in the concentration of the particles with increasing height, which is due to the action of gravity on the particles, and which is completely analogous to the decrease in the density of the atmosphere with increasing height above the earth (the so-called "sedimentation equilibrium"). Both cases involve an equilibrium between the dispersive effect of the thermal pressure and the downward-pulling action of gravity. The well-known formula for barometric height can be directly applied to colloidal sols with but slight modification. For the sake of clearness, the derivation of the formula will be briefly described.

In an upright column (area of the base = 1 cm²) of gaseous or dissolved particles the increase of hydrostatic pressure dP_1 is determined merely by the weight of the particles contained in a cylinder of the height dh. If the weight of a single particle is G' and the number per cubic centimeter is N', then dP_1 is given by

$$dP_1 = N'G'dh$$

For the thermal (osmotic or gas) pressure we have

$$P_2 = \frac{nRT}{v} = \frac{N'}{\mathbf{N}}RT$$

and

$$dP_2 = \frac{RT}{\mathbf{N}}dN'$$

At equilibrium, dP_1 and dP_2 must be equal, hence

$$\frac{dN'}{N'} = \frac{G'\mathbf{N}}{RT}dh,$$

from which results

$$ln\frac{N_1'}{N_2'} = \frac{G'\mathbf{N}}{RT}(h_1 - h_2) \tag{150}$$

or

$$\frac{N_1'}{N_2'} = e^{\frac{G'\mathbf{N}}{RT}(h_1 - h_2)} \tag{150a}$$

The "effective" weight G' of a gas molecule is simply $g\ m$ (g = the acceleration due to gravity), but for particles dissolved or suspended in a liquid the buoyancy of the liquid affects the "effective" weight of the particle, so that G' becomes

$$G' = g\ m\left(1 - \frac{\partial_1}{\partial_2}\right) = g\ v'(\partial_2 - \partial_1), \tag{151}$$

where ∂_2 is the density of the solid and ∂_1 that of the liquid, and v' is the volume of the individual particle.

Equation (150) was used first by Perrin, later by Svedberg, Westgren, and others to determine **N**.

Perrin used gamboge particles suspended in water for many of his researches. One of the greatest difficulties was to obtain a sufficiently homogeneous suspension with particles of approximately the same size.[1]

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[1] * Shaxby (see Table 2) avoided this difficulty by using certain bacteria as the suspended particles, although he did not work with the sedimentation method.

Perrin finally obtained such suspensions by careful, fractional centrifugation. By suitable choice of the velocity and time of centrifuging, the suspension would contain only particles below a certain size, while all the rest were precipitated, after centrifuging a number of times the dimensions of the particles would be brought within sufficiently narrow limits. The weight G' was calculated either by determining the mass m by counting a weighable number of particles, or by means of Eq. (151) by determining the volume v'. The latter could be found by several methods, of which measuring the diameter of the particle under the microscope was the most direct. The picture of a sufficiently homogeneous suspension, observed from the side, is shown in Fig. 38. When the number of particles N_1' and N_2' has been counted at two layers differing in height by $(h_1 - h_2)$, sufficient data have been obtained to calculate **N**. The mass m of the particles used by Perrin was between 2.0 and 2.5 10^{-14} g, which, although it seems to be very small, is still very large in comparison to ordinary chemical molecules, for these particles correspond to a molecular weight of about $10^{10}(O_2 = 32)$. The remarkable difference between the size of an ordinary gas molecule and a visible colloidal particle is most distinctly shown in the sedimentation equilibrium by the difference of height, which for a definite ratio $\frac{N_1'}{N_2'}$, is inversely proportional to the molecular weight or to the quantity G'**N**. For example, Perrin found that for $\frac{N_1'}{N_2'} = 2$ the difference in height $h_1 - h_2 = 30\mu = 0.003$ cm, while the corresponding difference for air molecules is about 5.5 km. For **N**, Perrin obtained a mean value of 6.82 10^{23}. More recent measurements by Westgren on colloidal gold and selenium particles gave a mean value of 6.05 10^{23}. The excellent agreement between these values and those obtained by other methods may be seen in Table 2, page 66.

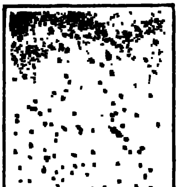

Fig. 38

* A common impression is that Perrin's formula (Eq. (150)) holds throughout the entire depth of a solution. This would be true if all the assumptions involved in Perrin's derivations are valid for suspensions. Actually, this is not the case, for Perrin's gamboge particles the concentration at a depth of 3 cm. would be 2^{1000} times that near the top of the suspension and even a casual observation shows that this is not true. PERRIN ("Atoms," translated by HAMMICK, D. Van Nostrand Co. (1923) p 99) states that heights of less than 0.1 mm. only are suitable for useful observations with the emulsions employed. WESTGREN (*Z. physik Chem*, **89**, 63 (1914)) has extended this to 1.1 mm. and approached the sedimentation equilibrium from both sides PORTER and HEDGES (*Phil Mag*, **44**, 641 (1922)) by taking into account the deviations from the gas laws due to the volumes of the particles, deduce

a formula which holds very well for a further distance of about 15 *mm*, the distribution of the particles throughout the main body of the suspension being sensibly constant.

* Perrin's derivation definitely assumes the applicability of the laws of perfect gases and these in turn require that there are no mutual force effects between the particles. Since this is by no means assured, it is clear that Perrin's law must fail at a depth where the concentration of particles has become so great that these forces are no longer negligible.

* It is also quite likely that no investigator has completely eliminated convection effects due to temperature fluctuations nor allowed a sufficient time for a true sedimentation equilibrium to be established throughout the entire body of the suspension. In fact the simple form of Stokes' law indicates that it would take one year for a gold particle ($d = 10\mu\mu$) to settle 3 *cm*. and this only in the complete absence of the complication of the Brownian movement and convection currents, and on the assumption that the particle does not combine with the solvent medium, which is doubtful.[1]

154. The Brownian Movement.[2]—As long as the particles of a solution, whether they be visible or not, are able to exert an osmotic pressure, they cannot be at rest, for, according to our fundamental conceptions, the osmotic pressure is due directly to molecular motion. The fact is that the motion of suspended particles was observed by the botanist Brown in 1827, long before any measurements of osmotic pressure were made. This trembling, irregular, translatory motion of suspended particles, which is usually called the "Brownian movement," remained unexplained until Einstein (1905), and at the same time Smoluchowski, discovered its relation to osmotic pressure and demonstrated that it was really a heat motion of the particles. The irregular motion observed under the microscope by no means corresponds to the true mean velocity of the particles, as the energy-distribution law demands, for according to this law (Eq. (83)) a particle with a molecular weight of 1×10^{10} must have a velocity $v = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.31 \times 10^7 \times 273}{1 \times 10^{10}}}$ = about 2.6 *cm./sec.*, while the path actually described in 1 *sec.* is only some thousandths of a millimeter. The difference means simply that the true path of the particle cannot be followed in an absolute sense. It consists of exceedingly rapid and small vibrations and the eye can recognize only the total displacement of the particle within a time of, at the very least, $\frac{1}{10}$ *sec.* (the time of the eye's accommodation), and this is merely the resultant of a number of actual displacements.

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[1] * We are indebted to our colleague, Prof A. W Thomas, for calling our attention to some of these points. See SVEDBERG, "Colloid Chemistry," p 101; BURTON, *Phil Mag*, **47**, 721 (1924), MASON and WEAVER, *Phys Rev*, **23**, 412 (1924).

[2] SVEDBERG, T "Colloid Chemistry," part II, Chemical Catalog Co. (1924); *Jahrb Radioakt Elektronik*, **10**, 476 (1913).

FURTH, R., *ibid.*, **16**, 319 (1920).

BURTON, E. F., "Physical Properties of Colloidal Solutions," chap. **IV**, London (1921).

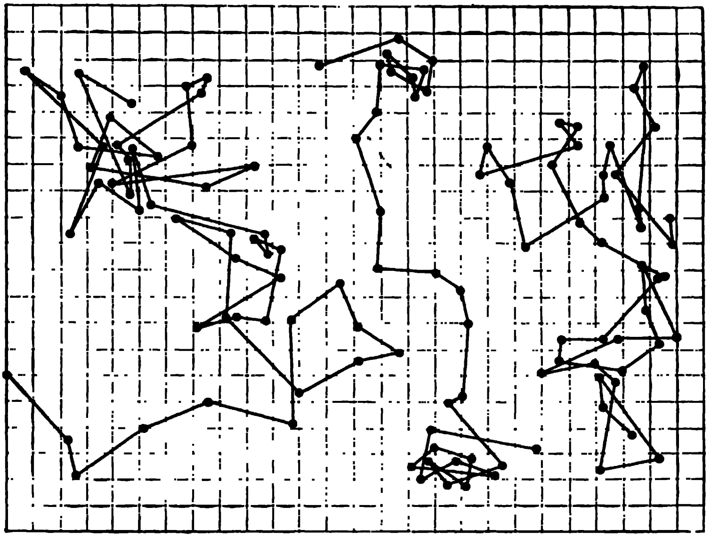

FIG. 39

The reason for the peculiar displacements actually observed in the Brownian movement, as Fig. 39 illustrates, can be explained as follows: A particle is subjected at all times to an enormous number of collisions with the rapidly moving molecules by which it is surrounded. The effect of these collisions is very largely annulled, since to a certain degree they take place equally on all sides. If the collisions are completely compensated, the particle merely vibrates at one point, but actually the compensation is not complete, so that the particle receives an excess impulse in one direction or another and therefore moves. The longer a particle is observed the greater is the probability that not all the collisions will be compensated. The observed displacement of a particle from its original position is thus the greater the longer it is watched, but, of course, it is not proportional to the time of observation t, but to $\sqrt{t}$ (see Eq. (153)). The gradual progression of particles taking place in this manner is usually called diffusion in ordinary solutions. Since, in the sense of the kinetic theory, there is no theoretical distinction between real (chemical) molecules and suspended particles or colloidal particles, the law of diffusion must be directly applicable to the latter also.

The progress of diffusion from a layer AB in both directions has already been discussed in **17** and is represented by Fig 12. The result obtained there has the following significance for the present case If a large number of particles are observed simultaneously, all of them at the time $t = 0$ being located on a straight line AB, then after a certain time t (say, 1 *sec*) a large number will still be found near AB, for their collisions with the liquid molecules have been largely compensated Another portion of them will have moved farther away from the zero line, but only a very small number will have traveled a relatively long distance. The average distances which the individual particles have moved forward, and which are called the *average displacements*, are represented by $\bar{x}_1$, $\bar{x}_2$, etc In order to take the progress in both positive and negative directions into account, it is convenient to use the square of the mean displacement, x^2 The calculation of this value consists in forming the expression $\frac{1}{n_0}\int_{x=0}^{x=\infty} x^2 dn$, in which Eq (37*a*) is to be substituted for dn This leads to the simple result,

$$x^2 = 2Dt \qquad (152)$$

or

$$D = \frac{x^2}{2t}, \qquad (153)$$

i e, the diffusion coefficient D of the particles can be calculated from observations of the square of the average distance passed over in a definite time t

155. Osmotic Pressure and Diffusion.—Since in the last analysis the osmotic pressure and the Brownian movement are nothing other than the two extremes of the same form of phenomenon, namely, the heat motion of particles, it must also be possible to find a relation between the diffusion coefficient D and the osmotic pressure. For the calculation a relatively rough, schematic treatment will suffice.[1]

As a first approximation, the particles may be supposed to be driven forward by the pressure force, and, indeed, in a liquid column of unit cross-section along which the osmotic pressure gradient is $\frac{dP}{dx}$, the osmotic pressure dP on the whole acts as a driving force on a particle in a layer dx in thickness, because on the one side is the pressure P, while on the other the pressure $P + dP$ acts in the opposite direction. But due to the friction to which the particles are subjected in the liquid, their velocities can increase only up to a certain limit. If this retarding frictional force is considered to be proportional to the velocity v of the particle, as in **14,** the total friction on $N'dx$ particles (present in a volume element $1 \times dx$) amounts to $fvN'dx$.

At equilibrium when the motion of the particle becomes uniform, *i e*, its acceleration has become zero, it follows that

$$N' \frac{d^2x}{dt^2}\, dx = -N'v_0 f dx + dP = 0,$$

or

$$\frac{dP}{dx} = N'fv_0. \tag{154}$$

In unit time $N'v_0$ particles are moved through the unit cross-section; this product is, therefore, identical with the term $\frac{dN'}{dt}$ of Fick's law (see **17**) if this refers to individual molecules and not to a gram molecular weight. Thus

$$\frac{dN'}{dt} = N'v_0 = D\frac{dc}{dx} = \frac{D}{v}\frac{dN'}{dx}. \tag{155}$$

Now according to Eq. (140):

$$dP = dN' \frac{RT}{\mathbf{N}v},$$

and it therefore follows from Eqs (154) and (155) that

$$\frac{RT}{f\mathbf{N}} = D. \tag{156}$$

The frictional force f acting on a particle may be calculated from its radius a and the coefficient of internal friction or viscosity ζ

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[1] Thus, for the present case P is identical with π in Eq 140.

of the liquid by means of a formula given by Stokes for spherical particles:

$$f = 6\pi\zeta a.$$

An exact test has shown that this formula holds quite accurately for friction in water down to particles which have radii of about those of sugar molecules, but correction factors are required for smaller radii. Since the direct measurement of the diffusion constant for visible particles is not very accurate, it may conveniently be replaced by the determination of the square of the mean displacement (Eq. (153)) which the particles experience during a time t. Finally, from Eq. (156) the following relation for **N** is obtained:

$$\mathbf{N} = \frac{RT}{3\pi\zeta a}\,\frac{t}{\Delta^2}, \qquad (157)$$

in which the right-hand side contains only experimentally measurable quantities. A number of investigators have determined **N** according to this method. Especially careful work was done by Nordlund[1] on mercury droplets, which gave a mean value of $\mathbf{N} = 5.9 \times 10^{23}$

The Brownian movement may also be observed in gases, for example, with oil droplets. In this case it is particularly rapid, since the internal friction of gases is considerably less than for liquids, but it is less suitable for the estimation of **N** because Stokes' law reaches its limit of accuracy at particles of considerably larger size than in liquids; this is due to the very much greater free path of the molecules in gases.

156. Density Fluctuations.—If the number of particles contained in a unit volume of a suspension or colloidal sol is determined from time to time, it is found that the number fluctuates, but a mean value N_m may be obtained if the observations are continued over a long period, the number N found at any instant nearly always deviates from this. From theoretical, probability considerations, it is possible to calculate the average percentage deviation $\bar{\varepsilon} = \frac{N - N_m}{N_m}$ of N from the mean value N_m.

Assuming that the particles do not exercise any force effects upon each other, the following formula, which is in good agreement with experiments on colloidal sols, is obtained:

$$\bar{\varepsilon} = \sqrt{\frac{1}{N_m}}. \qquad (158)$$

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[1] * Cited by SVEDBERG, T., "Colloid Chemistry," *loc cit*, p. 118.

On the basis of this formula, density fluctuations must also occur in gases, but these would be perceptible only if a very small volume could be observed. For example, in order to obtain a mean density fluctuation of 1 per cent the actual number of molecules N_m must be less than 10,000, the corresponding volume v_0 for a gas under atmospheric pressure is only

$$v_0 = \frac{22410 \times 10^4}{\mathbf{N}} = 4 \times 10^{-16}\ cm.^3, \qquad (159)$$

which is a cube with an edge of $7 \cdot 10^{-6}$ *cm.* = 70$\mu\mu$. Still these density fluctuations have an effect so that gases are not entirely homogeneous but somewhat "turbid." To be able to demonstrate this turbidity optically, it is, of course, necessary to have considerably thicker gas layers or very strong light intensity. The earth's atmosphere illuminated by the sun satisfies these conditions We observe the effect of this turbidity as the blue color of the sky, disregarding the cloud particles and similar suspended matter, without this effect the sky must appear black. From the intensity of the blue color in comparison to the direct sun rays, it is possible to draw some conclusions as to density fluctuations in the air, on the basis of a theory developed by Lord Rayleigh. It is thus theoretically possible to determine the volume v_0 in which a definite density variation occurs by optical means, and then by means of Eq (159) to calculate the Avogadro number **N**. This method, however, is extremely sensitive towards the turbidity of the air caused by water droplets, dust, etc., and thus gives a value for **N** which is somewhat too small.

157. Formation of Hydrates (Solvation).—The fact that substances go into solution spontaneously (neglecting exceptional cases) indicates that work can be performed by this process (**30**) and that, therefore, an affinity exists between solute and solvent. From the standpoint of molecular theory this can be explained only by assuming that some sort of forces act between the molecules of the solvent and the molecules of the substance dissolved. On the whole, the nature of these forces is certainly not known very exactly at present. In numerous cases, however, electrical forces are involved (see **191***a*, **244**). Now since these forces, like all molecular forces, probably have only a relatively short range of action (*e g* , see **172**), it might be expected that around the individual dissolved particles a number of solvent molecules would be fixed more or less firmly This process is usually called *hydration* when aqueous solutions are involved, *solvation* being the general term.

A number of experimentally established facts can be explained qualitatively quite well on the assumption that hydration takes place, but quantitatively the results of the various methods for determining the degree of hydration, the number of solvent molecules associated with each solute molecule, agree only imperfectly up to the present. This may be due mainly to the solvent molecules being held with different orders of strength, those nearest the solvent molecules being more firmly held than those farther away, and therefore a sharp distinction between bound and unbound solvent molecules may not be possible.

In the formation of colloidal sols not only the combination of the colloidal particle with solvent molecules, but also its combination with dissolved molecules or ions plays an important part, so that it seems appropriate to designate the group—colloid particle + attached solvent molecules + attached dissolved molecules—by a special term "micelle," as suggested by Zsigmondy.

The kinetic calculation of the osmotic pressure is not affected by hydration, however, since the osmotic pressure is dependent only upon the number and mean kinetic energy of the freely moving particles, and not their masses. Hydration changes the mass but not the other two quantities, as follows from the energy-distribution law.

d. APPLICATIONS

***158. Molecular-weight Determinations of Dissolved Substances.**—Since the molecular weight of a solute always enters into the derivation of the formulas for the colligative properties of a solution, and since it can be shown on kinetic grounds that these properties depend upon the number of dissolved particles, at least for dilute solutions, it follows that any one of the colligative properties will serve for the determination of the molecular weight of a substance in solution. In fact, van't Hoff's demonstration that the gas laws could be applied to the determination of the molecular weight of dissolved non-volatile substances, just as though they were gases, forms the basis for a large part of the development of present-day physical chemistry.

* As a rule, the freezing-point method is the most simple experimentally and yields the most accurate results,[1] though in special

cases the elevation of the boiling point[1] or depression of the vapor pressure[2] may be necessary or preferable.

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[1] * See ADAMS, *J. Am. Chem Soc*, **37**, 481 (1915); HALL and HARKINS, *ibid.*, **38**, 2658 (1916), for description of apparatus and technique.

By a procedure exactly analogous to that given under the boiling-point law, Eq. (148) may be simplified to

$$-\Delta T_M = \frac{M_1}{1000}\,\frac{RT_M^2}{\Lambda_f}\,C_2, \tag{148a}$$

where the term $k_F = \frac{M_1}{1000}\,\frac{RT_M^2}{\Lambda_f}$, which is the **molal freezing-point constant,** has the value 1.858° for aqueous solutions.

*A known weight of solute X_2 is dissolved in a solvent and the depression of the freezing point of the solvent by this addition noted with a Beckmann thermometer or by the use of a thermocouple. The ratio $\frac{\Delta T_M}{k_F}$ gives the molality of the solution, from which it is easy to calculate the molar weight, knowing the weight of X_2 dissolved in 1000 g. of solvent. It should be remembered that Eq. (148a) is approximate even when components which are sufficiently alike to conform to the requirements of **(141)** are employed, and should therefore be used only in dilute solution. A more exact form, retaining the composition in terms of mole fraction, can be derived from Eq. (147b) by expansion in series and, after introducing the proper values for the constants of an aqueous solution, becomes

$$X_2 = 0.00969(\Delta T_M - 0.00425\,\Delta T_M^2) \tag{147d}$$

or, by rearrangement,

$$-\Delta T_M = 103.20(X_2 + 0.428\,N_2^2). \tag{147e}$$

Equations (147d) and (147e) are accurate to 0.001° up to ΔT_M = 7°, when the solute forms an ideal mixture with water (*i.e.*, to about 3.5 molar) and should be used in preference to Eq. (148a) for concentrated solutions.

*If desired, the osmotic pressure may be directly calculated from the freezing point by an equation corresponding in form to Eq. (147d); namely,

$$\Pi = 12.06(\Delta T_M - 0.00178\,\Delta T_M^2) \tag{145d}$$

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[1] * Cottrell, *J. Am. Chem. Soc.*, **41,** 721 (1919).

[2] * See Menzies, *Z. physik. Chem.*, **76,** 231 (1912), Frazer and Lovelace, *J. Am. Chem. Soc.*, **36,** 2439 (1914), and **45,** 2930 (1923), for references to other papers and for details of the method.

8. THE EQUILIBRIUM BETWEEN STATES OF AGGREGATION IN THE PRESENCE OF OTHER SUBSTANCES

a EMPIRICAL FOUNDATIONS

159. The Distribution Law.—As the limiting case of equilibrium between two substances, the solution of a gas in a liquid may be considered first In this case, provided complications, such as chemical changes, are avoided, the absorption law of Henry-Dalton (1803 and 1807) is valid. This law in its simplest form states that *the amount of a gas dissolved in a liquid is proportional to the partial pressure of the gas*, or at a given temperature the ratio of the concentration of the substance in the solution c_1 to the concentration in the gas c is a constant.

$$\frac{c_1}{c} = S_1. \tag{160}$$

Nernst calls the proportionality factor S_1 the **solubility coefficient.** The law does not hold if the gas changes its molecular state in the solution and it is attempted to compare the concentration in the solution with that in the gas in spite of the change (further, see **197**). However, the law remains correct if it is applied to each molecular species present, thus obtaining a different value of the solubility coefficient for each one (Nernst, 1891).

If a single molecular species has the opportunity to dissolve simultaneously in two immiscible liquids, then the Henry-Dalton law holds for both solutions, and besides Eq. (160) we have also $\frac{c_2}{c} = S_2$. By combining the two we get

$$\frac{c_1}{c_2} = \frac{S_1}{S_2} = Const. = S_{1,2} \tag{161}$$

In words, this means that the molecular species distributes itself between the two liquids in such a way that the relation of the concentrations is constant; $S_{1,2}$ is called the **distribution** or **partition coefficient.** The applicability of this law is by no means limited to the substances which are gaseous under ordinary conditions, but also embraces any non-volatile substance. Essentially, the difference between an easily and a difficultly vaporizable substance is only that the concentration of the latter in the vapor phase is very small, and therefore the solubility coefficient is relatively large. Yet the distribution coefficient, as Eq. (161) indicates, does not depend upon the absolute values of S_1 and S_2 but upon their mutual ratio. The assumption involved in the exact application of the *simple* distribution law (Eq. (161)) is, of course, that the distributed substance is in the "dilute" state in all phases, so that the gas law $pv_m = RT$ is valid, whether for the partial pressure of the gas or the osmotic partial pressure. Only in such a case can Eq (161) be derived thermodynamically. (Cf. **188b.**)

With increasing temperature the solubility coefficient usually increases but this statement is not without exceptions. Nothing general can be stated concerning the distribution coefficient beyond that given in **147, 148,** and **149,** since S_1 can increase more or less rapidly than S_2.

In the *general case,* the concentrations of the substances in the different phases are no longer proportional to each other but are always definitely determined by the concentration c_1 of the substance in the one phase as well as the pressure, temperature, and concentrations in the other phases, c_1', c_1'', etc, or, what amounts to the same thing, there are in all cases functions of the type:

$$\begin{aligned} c_1' &= f(p,T,c_1) \\ c_1'' &= \varphi(p,T,c_1), \text{ etc.} \end{aligned} \tag{162}$$

The simplest example of such a function is the vapor-pressure curve, but here, of course, the pressure is no longer an independent variable, since equilibrium between vapor and liquid is possible at only one pressure for each temperature.

On the other hand, if a liquid whose vapor had at the beginning a concentration c_0, is brought into contact with a difficultly soluble gas and with a total pressure P acting on the system, this is an example of an equilibrium which is dependent on both temperature and pressure and in which the concentrations in the two phases are not proportional to each other. The effect of increase of pressure is to increase the concentration (partial pressure) of the vapor. The density of the liquid increases but slightly during this process, especially if its compressibility is small. It may be supposed that the effect of the pressure transmitted to the liquid by means of the difficultly soluble gas is to squeeze a part of the liquid molecules out into the gas space where they find a better opportunity of existence among the gas molecules than among the more densely packed liquid molecules.

The pressure thus exercised upon the liquid acts in just the opposite direction to the osmotic pressure, since the pull of the liquid molecules towards the interior of the liquid is strengthened. However, except for the direction, the effect of this external pressure is exactly the same as that of the osmotic pressure In order to secure a mathematical relation for a vapor pressure increase resulting from an external pressure transmitted by a foreign gas, the thermodynamic reasoning followed in **143** can be repeated without being changed. *In this way we arrive at Eq. (144c), in which for the present case P the external pressure, equals Π. Substituting the concentrations c' and c_0 of the compressed and uncompressed vapors for p and p_0 and the concentration of the liquid c for $\frac{1}{V_0}$ we get

$$\Pi = -cRT\,ln\frac{c'}{c_0} \quad \text{or} \quad P = cRT\,ln\frac{c'}{c_0}\cdot \tag{163'}$$

*In the limiting case when c' and c_0 are nearly equal this reduces to

$$\frac{c'-c_0}{c_0} = \frac{P}{cRT} \tag{163)^1 \quad (163$}$$

since under these circumstances

$$ln\frac{c'}{c_0} = ln\left(1 + \frac{c'-c_0}{c_0}\right) = +\frac{c'-c_0}{c_0}.$$

In this, corresponding to the general function (Eq (162)), c' is actually dependent upon P, T, and c (c can be varied by diluting the liquid by another liquid).

160. Gibbs' Phase Rule.—A rule of extreme importance and general applicability can be derived from the fact just discussed that there exists a definite and absolute relationship between the concentrations of substances in various phases. This is **Gibbs' phase rule**; it fixes the relation between the number of phases which are capable of existing, the number of chemical substances present in the system, and the conditions of temperature and pressure.

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[1] *The derivation of Eq. (163) differs slightly in form from that given in the German text because of the changes that have been introduced in **143–149.**

* Two terms will be constantly used in connection with this rule, "phase" and "component," and it will be best to define them at once. The term "phase" has already been defined for chemically homogeneous substances in **110,** but a somewhat more descriptive definition may now be quoted:

> A heterogeneous system is made up of different portions, each in itself homogeneous but marked off in space, and separated from each other by boundary surfaces. These homogeneous, physically distinct, and mechanically separable portions are called **phases.**

* While the conception of a phase involves no difficulty, the same is not true of the term **component.** At first, it would seem as if each chemical substance would be a component, but this is only partly correct Only those substances, the concentrations of which can be varied independently in the different phases can be called components. Findlay gives the following definition:

> As the components of a system, there are to be chosen the smallest number of independently variable constituents, by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation.

*It will be seen at once that this definition permits a certain amount of arbitrariness in choosing which of the chemical substances shall be considered as components, especially when the number of components is three or more.[1]

In deriving the phase rule it will first be assumed that a total of n chemically different substances takes part in the equilibrium. These will in some way or other distribute themselves among various phases, and it will be assumed that in at least one phase a perceptible, even though slight, amount of each substance is present. In general, it may be assumed that this takes place in either the liquid or the gaseous phase. If no phase is present in which the various substances exist simultaneously and in which they are able to interact, then equilibrium cannot take place and the phase rule loses its meaning.

For each of the homogeneous phases present there is an equation of state analogous to those already discussed extensively for a number of pure substances Since the general case involves a number of substances in each phase, the equation of state is no longer merely a relation between pressure, temperature, and total volume, but in place of the total volume we have the concentrations of the individual substances in the particular phase under consideration. The "state" of a phase is thus defined by the pressure, temperature, and concentrations of substances in this phase. Between these quantities there must be an exact relationship, the **generalized equation of state.** It is easily seen that the existence of such an equation of state for a system containing several substances is just as necessary as for a system with only one substance.

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[1] * For a further discussion see FINDLAY, "Phase Rule," p. 7, Longmans, Green & Co. (1923); see also **198.**

For example, an unsaturated solution contains given amounts of a number of substances dissolved in a liquid; the solution will then assume a definite volume at a definite temperature and pressure exactly like a pure liquid, but the volume of the solution determines the concentrations of the dissolved substances. For each homogeneous phase in which all n components are present there is a definite relation

$$F(p, T, c_1, c_2, c_3, \qquad c_n) = 0, \tag{164}$$

In the remaining phases not all the n components need be present and we might have

$$F'(p, T, c_1', c_2', c_3' \qquad) = 0 \tag{164a}$$
$$F''(p, T, c_1'', c_2'', c_3'', \qquad .) = 0. \tag{164b}$$

We now apply Eq. (162) which holds for the individual substances 1, 2, 3 . . . n and the different phases, and with its help eliminate the terms $c_1', c_2', c_3', c_1'', c_2'', c_3''$, etc. from (164*a*), (164*b*), etc., thus obtaining besides Eq. (164) and instead of Eqs. (164*a*), (164*b*), etc. a number of equations of the form

$$\Phi(p, T, c_1, c_2, c_3 \qquad) = 0 \tag{164c}$$
$$\Psi(p, T, c_1, c_2, c_3 \qquad) = 0, \tag{164d}$$

in which, besides p and T, only c_1, c_2, c_3 are still present as variables.

If there is a total of n components, then $n + 2$ equations or, if each equation corresponds to one phase, $n + 2$ phases are required to fix all the variables (n concentrations, p, T). Conversely, only at definitely fixed values of the concentrations, pressure, and temperature can $n + 2$ phases coexist. Such a system is called *non-variant* or *invariant* and is exemplified by any single substance or one-component system when three of its phases are in contact. This point is, therefore, called the **triple point.** If two components are present, then four phases are in equilibrium with each other at a **quadruple point.** The more complicated systems have a number of triple, quadruple, etc. points. Examples of the occurrence of several triple points have already been given in the diagrams for sulfur and ice (Figs. 30 and 31).

Now, if only $n + 1$ phases are at the disposal of the n components, then not all of the $n + 2$ variables will be fixed. One of them, pressure, temperature, or *one* of the concentrations, can be arbitrarily determined. Such a system is said to have one **degree of freedom** and is called *univariant.* In the same way a system with only n phases is divariant and has two degrees of freedom.

TABLE 27

Number of components	Degrees of freedom	Number of phases	Geometrical representation of the system
1	0 (invariant)	3	A point (triple point) in the p, T-plane
1	1 (univariant)	2	Curves (vapor-pressure, sublimation-pressure, and melting-point curves) in the p, T-plane which intersect at the triple point.
1	2 (divariant)	1	Areas of the p, T-plane which are separated by the curves of the univariant systems.
2	0 (invariant)	4	A point (quadruple point) in the p, T, c-space[1])
2	1 (univariant)	3	Curves in space, intersecting in the quadruple point.
2	2 (divariant)	2	Surfaces which connect the space curves.
2	3 (trivariant)	1	Sections of the solid (space) diagram which are separated by the surfaces of the divariant systems.

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[1] The new variable c generally signifies the ratio of the concentrations of the two components

If n is the number of components, P the number of phases, and F the degrees of freedom, then all possible cases may be summed up in the following general statement of the phase rule:

$$P + F = n + 2. \tag{165}$$

The application of the phase rule to one- and two-component systems may be best illustrated by geometrical representations Table 27 contains a summary of the various possibilities in such systems.

For more than two components even the three-dimensional space diagrams are no longer sufficient for a complete representation of the system, and projections must be used. In three-component systems the pressure and vapor phase are frequently of minor importance, in which case the prevailing relationships, similar to two-component systems, can be represented by three-dimensional diagrams of which one coordinate represents the temperature and the other two the concentration ratios

161. Application of the Phase Rule to Two-component Systems.[1]—For one-component systems several examples corresponding to Table 27 have already been introduced in **120** and Figs. 30 and 31. In two-component systems the number of possibilities is already so great that only a few typical cases which are free from complications can be considered here. For further illustrations special books on heterogeneous equilibrium and textbooks on the phase rule or metallography must be consulted.[2]

In numerous cases, especially melting and transition phenomena, it is possible to neglect the pressure variable, *ie.*, consider the system at constant pressure,[3] and therefore represent the relations on a plane diagram. The coordinates then represent the temperature as ordinate and the concentration ratio or the concentration of one component as abscissa. The individual bounded areas on Figs. 40 to 47 generally represent the range of existence of *one* phase; along the boundary curves two phases are in equilibrium. But not every point on the planes represents one definite phase because frequently a decomposition into two phases takes place. Such areas are shaded in Figs. 40 and 43 to 47.

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[1] The diagrams presented here are in a large part taken from Goerens, "Einfuhrung in die Metallographie," 3rd and 4th Eds , Halle (1922)

[2] * Findlay, A., "Phase Rule and Its Applications," Longmans, Green & Co. (1923), Desch, C., "Metallography," Longmans, Green & Co (1922), Clibbens, D , "Principles of Phase Theory," The Macmillan Company (1920), and especially Roozeboom, Backhuis, "Die heterogenen Gleichgewichte," Vieweg, Braunschweig.

[3] * Experimentally, this is what is actually done in almost every case Such systems are called *condensed systems* and for them the formal statement of the phase rule becomes $P + F = n + 1$. The study of such systems forms a very important part of metallography (See Clibbens, *loc. cit* for a detailed discussion of these systems)

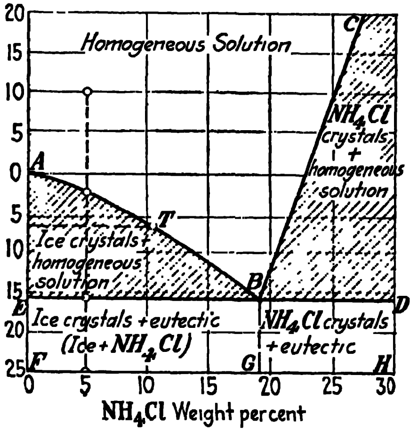
20
15
10
5
0
5
10
15
20
25
Homogeneous Solution
C
NH_4Cl crystals + homogeneous solution
A
T
Ice crystals + homogeneous solution
B
E
D
Ice crystals + eutectic (Ice + NH_4Cl)
NH_4Cl crystals + eutectic
F
G
H
0 5 10 15 20 25 30
NH_4Cl Weight percent

FIG. 40

162. Typical Melting Diagrams of Two-component Systems. 1. *Simple Eutectic Mixtures.*—If a very dilute solution, such as an ammonium chloride solution (Fig. 40), is cooled, pure ice begins to separate when the temperature reaches a point just below 0°C. The solution thus becomes more concentrated and the freezing point of the remaining liquid decreases more and more, following along the curve *AB*. At first, the depression of the freezing point of the solution, obeying Raoult's law (see **148**), is proportional to the concentration and the curve *AB* is a straight line, but later deviations from this law usually occur. Thus, along *AB* a solution of *m* per cent NH_4Cl is in equilibrium with pure ice.

Upon continuing the cooling, a point *B* is finally reached at which the solution is saturated with respect to NH_4Cl. This point is, therefore, a quadruple point, since the solution, ice, NH_4Cl, and, at sufficiently low pressure, the vapor, all coexist in equilibrium. The quadruple point in which two different crystal substances are in equilibrium with a melt and the vapor at a temperature which is lower than the melting point of either of the pure components is called the **eutectic point.**[1] The mixture which crystallizes at this point is called the **eutectic mixture** or simply the **eutectic.** It will be seen at once that a solution which originally had the composition of a eutectic mixture would solidify at the eutectic point since further displacement of the freezing point is impossible and in this respect behaves like a pure substance. However, an examination of the solid which separates shows immediately that it is a mixture of different crystals.

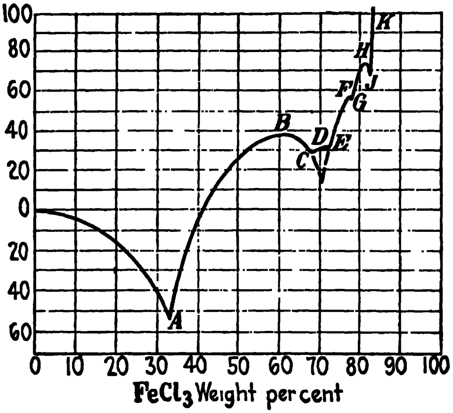

FIG. 11

The curve *CB* represents the relation between the solubility of NH_4Cl and temperature. Upon cooling a saturated solution of NH_4Cl, the pure salt will separate along the branch *CB* just as ice separates along *AB*. The solubility curve *CB* must also end at the same point as the equilibrium curve *AB*, *i.e.*, at the eutectic point *B* at which both ice and NH_4Cl separate together.

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[1] * In aqueous systems this is frequently called the *cryohydric point.*

As already mentioned, the shaded areas on the diagrams correspond to inhomogeneous phases. If a 5 per cent solution of NH_4Cl is brought to a temperature of −7.5° (*i.e.*, if it is attempted to get within the area *ABE*), a solution of the composition at the point *T* is formed with the corresponding amount of ice. In the area *EBGF*, ice and a certain amount of the eutectic is present, and in *BDHG* solid NH_4Cl and the eutectic.

A further example of a simple eutectic mixture is given by the system lead-silver, for which the portion of the melting diagram around the eutectic point is given in Fig 50.

2. *Formation of a Compound.*—Next, the case where the two components can combine to form a chemical compound in the liquid as well as in the solid state may be considered. As far as the melting phenomena are concerned, the compound behaves in the same way as a pure component; by adding any other substance its melting point is lowered. Therefore, the melting point of a chemical compound is located at a maximum which lies between two eutectic points on the melting curve. (*Example:* The system *Sn* − *Mg* (Fig. 42).)

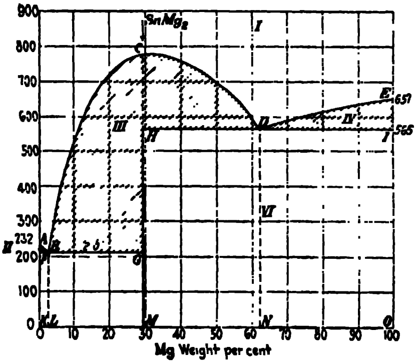

Fig. 42.

In many cases two components are able to form a whole series of different compounds. As an example of this, the system $FeCl_3 - H_2O$ (Fig. 41) may be used. At the points (maxima) *B*, *D*, *F*, and *H* the hydrates $FeCl_3.6H_2O$, $2Fe_3Cl.7H_2O$, $2FeCl_3.5H_2O$, $FeCl_3.2H_2O$ are formed.

Quite often one of the eutectic points is displaced in such a way that the maximum vanishes (often called *hidden maximum*) and only a small "break" or discontinuity in the curve can be observed (see Fig. 43 for the system Na — K). This break occurs when the compound formed exists only in the solid state and not in the melt. In other words, the compound becomes unstable before reaching its melting point If the solid compound Na_2K is warmed, a decomposition sets in at the point *D*. Thus a liquid is formed with a composition corresponding to the point *C* (therefore somewhat richer in K than the original solid) and at the same time pure Na crystals are formed If the heating is continued the Na crystals gradually melt, thereby enriching the liquid with respect to Na, and the melting point increases along the curve *CA* until the entire substance is melted at the point *B*. (Cf. **149.**)

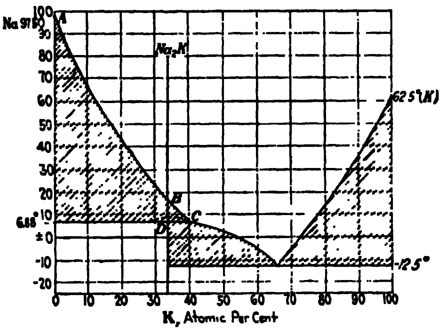

FIG 43

3. *The Formation of Solid Solutions.*—A very important case in metallography occurs when both components crystallize out together in all proportions or, what amounts to the same thing, form a solid solution with each other. Thus, molecularly, they are completely homogeneous even in the solid state without being chemically bound. On the whole, no eutectic (quadruple) point can exist in this case, since the solid solution represents only a single phase. A typical diagram for this case is that of Ag — Au (Fig. 44). If a gold-silver alloy with about 45 per cent Ag is cooled from the liquid state, the separations of crystals begins at *A*. The solid solution phase does not, however, have the same composition as the liquid from which it separates, but is always somewhat richer in the higher melting component. In the above

example the composition of the solid first separating is about 28 per cent Ag and 72 per cent Au, corresponding to the point B.

While the separation continues, the melting point decreases along the curve $AA_1A_2A_3$. Two theoretically different cases must be differentiated:

In the first case, cooling takes place very slowly and the crystals have the opportunity to reach equilibrium with the liquid phase at every moment. Then by progressive separation the whole mixed crystal will have the compositions corresponding to the points B, B_1, B_2, while the composition of the liquid will have the

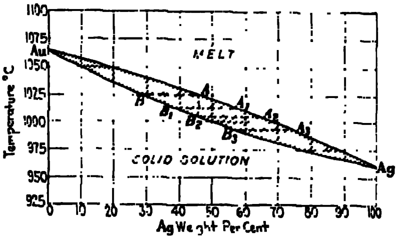

FIG. 44.

corresponding compositions A, A_1, A_2. As soon as the melt has cooled to the point A_2 and therefore the solid has reached the composition of the original liquid B_2, the whole mixture must be solidified.

On the other hand, if the cooling has taken place rapidly, only the surface of the solid will be in equilibrium with the liquid and the interior will have another composition. If, for example, the composition of the original liquid was A, the first solid which is now the nucleus of the crystal has the composition B. Since upon rapid cooling the liquid passes through the points A, A_1, A_2, A_3, a series of layers having compositions corresponding to B, B_1, B_2, B_3 are formed. Solidification can cease only when the liquid and crystal surfaces have the same composition; this occurs, as the diagram shows, at the melting point of pure silver.

Depending upon the rapidity of cooling and other experimental conditions, all possible stages between these two limiting cases can be obtained. Since during the "freezing out" a certain amount of separation of the components occurs, this *liquation* *process* is sometimes used in technical practice to separate or at least to concentrate individual constituents of a mixture.[1]

4. *Incomplete Miscibility.*—The case in which the two components do not form mixed crystals in all proportions, but which has a "miscibility gap" in its diagram, may be considered as a combination of the two cases 1 and 3. (*Example:* The system Al — Zn (Fig 45).) If a liquid of any composition is cooled, the phenomena are theoretically the same as depicted under case 1; however, no pure components separate but only solid solutions which, depending upon the velocity of cooling, may be in equilibrium with the liquid only at its surface or throughout the entire crystal. However, the point *C* cannot be passed from either side since at this point the entire liquid solidifies. Both mixed crystals of the compositions *A* and *B* separate, and *C*, therefore, is a eutectic point. Towards lower temperatures below the eutectic point (or, better, the eutectic temperature) the range of existence usually, but not in this case, becomes smaller, *i.e.*, the miscibility gap becomes greater.

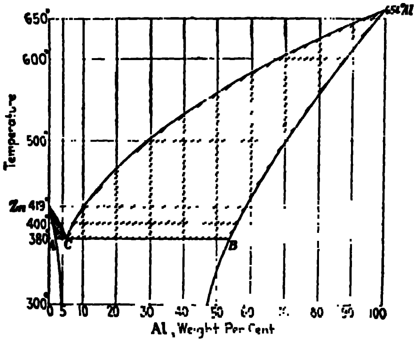

FIG. 45.

163. Mutual Solubility of Two Liquids.—Of the numerous other possible states in which two-component systems can exist, only that of the coexistence of two liquid phases will be discussed.

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[1] * The X-ray analysis (see **357**) has given considerable information as to the structures of solid solutions. See BAIN, *Chem. Met. Eng.*, **28**, 21 (1923), JEFFRIES and ARCHER, *ibid*, **29**, 923 (1923); VEGARD, *Z. Physik.*, **5**, 19 (1921); WESTGREN and PHRAGMÉN, *Nature* (Jan. 26, 1924); also footnote to **173**.

At low temperatures many pairs of liquids, such as phenol and water, are only soluble to a limited extent in each other. By shaking together two such liquids, two liquid phases are formed: (1) a saturated solution of liquid I in liquid II, and (2) a saturated solution of liquid II in liquid I (see Fig. 46 and discussion in **146**). Metals also form such *two-layer* system, *e.g.*, the system $Pb - Al$. If the temperature is increased, the mutual solubility usually increases also and the two liquids become more and more similar.

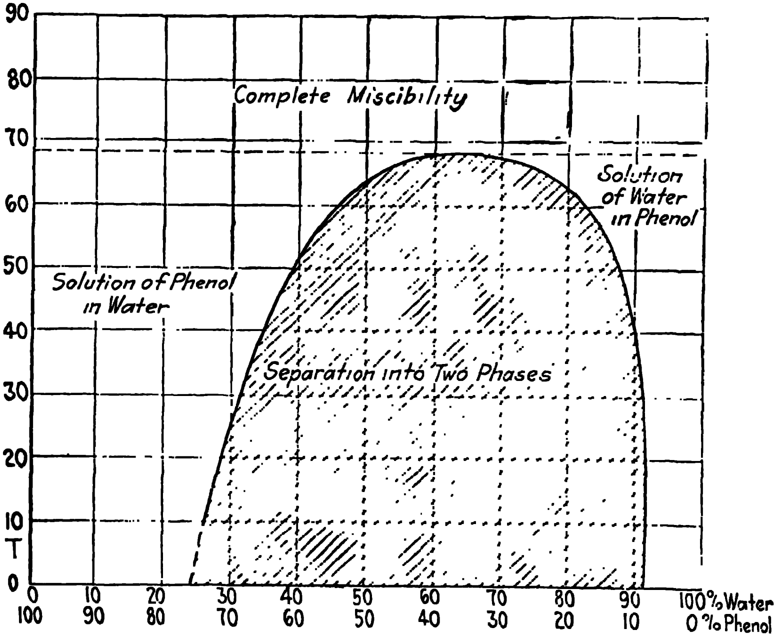
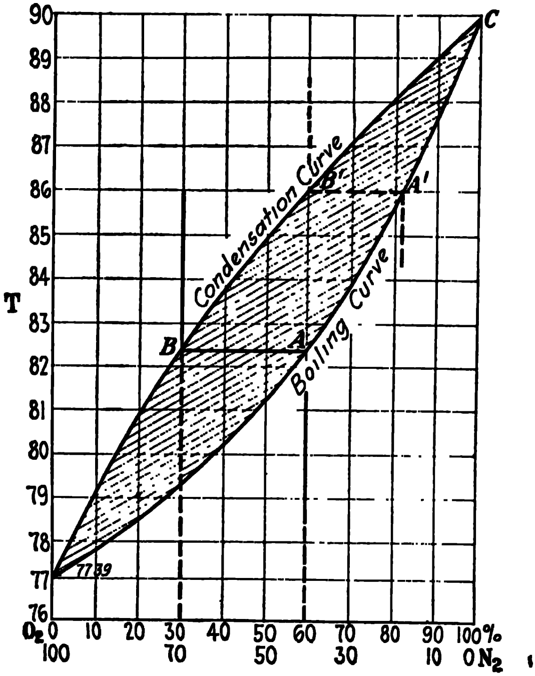


FIG. 46.

Finally, a point is reached at which the difference entirely disappears. The two layers are then identical and there is only *one* phase. This phenomenon corresponds completely to the transition gas-liquid at the critical point. Correspondingly, when the mutual solubility is represented as a function of temperature, somewhat the same picture is obtained as in the Mathias' rule (compare Figs. 46 and 29).

164. Evaporation and Condensation of Mixtures.—We may also briefly discuss the equilibrium between a two-component system and its vapor, in which there is but one liquid phase and one gaseous phase and which, therefore, according to the phase rule, is divariant. In order that the simplest possible representation may be used, it is best to fix one of the variables. Practically, it is most convenient to fix the pressure so that the temperature becomes a function of the composition of the solution; in other words, the boiling point is investigated as a function of the composition.



(a)

FIG. 47a

From the very great number of possible systems only the simplest and most important technical cases can be chosen for discussion at this point and may be illustrated by the concrete examples in Figs. 47*a* and *b*.

Figure 47*a*.—A liquid mixture of nitrogen and oxygen containing 60 per cent O_2 and 40 per cent N_2, which boils at 82.5 *abs.* under 760-*mm.* pressure. However, the vapor existing in equilibrium with this phase does not have the composition of the point *A* but that of an equally high point *B* (70 per cent N_2 and 30 per cent O_2). Conversely, if a gaseous mixture of 60 per cent O_2 and 40 per cent N_2 is cooled, a liquid containing more than 60 per cent O_2 and corresponding to the point *A′* is obtained. This pair of substances, similar to solid solutions, thus has two curves, one boiling curve and one condensation curve, enclosing an area between them in which no homogeneous phase exists.

Figure 47b.—If one of the curves passes through a maximum or minimum (a well-known example of the former is the system

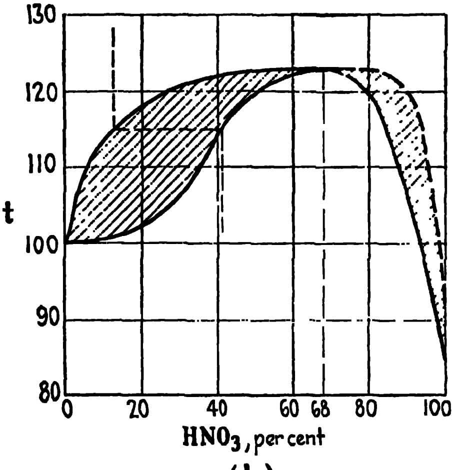


FIG 47*b*.

$H_2O - HNO_3$), then the other curve must behave similarly at the same point. To every point on the condensation curve there must be a corresponding point at the same level on the boiling curve. It can easily be seen that this condition would not always be fulfilled if the condensation curve possessed a maximum while the boiling curve did not. Therefore, at the maximum the composition of the liquid and the vapor are the same, so that at this point the mixture behaves as a simple chemical substance. However, the conclusion that a chemical compound exists at this maximum is as little justified as in a eutectic mixture, which freezes at a constant temperature without change of the gross composition.[1]

165. Apparent Limitations of the Phase Rule.[2]—It must be emphasized at this point that the phase rule is applicable only when the system is really in equilibrium. In nature, labile states frequently occur which can maintain themselves for long periods of time (the so-called "false equilibria") and which are very difficult to distinguish from real equilibria. Excellent examples of the formation of such labile states are found among fused mixtures of silicates which show a decided tendency to form "glasses" and remain labile for long periods even at high temperature. The metallic alloys also frequently exhibit labile states which are often of industrial importance. The rapid cooling of a solution of roughly 1 per cent of carbon in iron results in a transition state with properties of the greatest technical importance (steel), and, although from the standpoint of the phase rule this state is unstable, at ordinary temperatures it may last for hundreds of years.

The application of the phase rule to the above cases depends largely upon whether or not the practical difficulties in determining the stability or instability of the system can be overcome, and, as such, involves no question of the theoretical application of the rule. There are, however, other special cases, which, of course, occur very rarely, in which the phase rule appears to fail even for real equilibrium, and the number of degrees of freedom may be greater or less than Eq. (165) demands.

An example of such a case would be offered by a substance existing in two allotropic modifications which can form a series of solid solutions. In this case the transition between the two modifications would not, as the phase rule requires, take place at a definite point (no degrees of freedom). If the difference between the allotropic modifications is considered as differences in the interior of the atoms or molecules, then every difficulty with respect to the phase rule is avoided, for we then have what really amounts to a two-component system. But if the atoms or molecules are the same, then allotropy can be due only to a difference in their arrangement in the crystal. According to the existing crystallographic knowledge, solid solutions cannot form under these circumstances, so that the transition from one allotropic form to another must take place at a definite temperature and not over a temperature interval. With respect to these considerations an interesting example is given by the transition between α-iron and β-iron, which, according to Westgren,[1] occurs within a temperature interval of 30 to 50° just below 770°C. without change of crystal structure. To bring this into agreement with the phase rule, the existence of two different kinds of iron atoms must be assumed. However, the facts may be represented more correctly by the conception that this is not a transformation in the sense of the phase rule. The peculiarity of this transformation consists in the loss of ferromagnetic properties combined with a heat effect, *i.e.*, in comparison with α-iron, β-iron is non-magnetic. This peculiarity can be explained according to a theory by Langevin, the basis of which is the conception that with increasing temperature the irregular heat motion destroys the elementary magnetons which are present, although they do not always have a direct outward effect, and thus a certain amount of magnetic (potential) energy is liberated and converted into work. The theory demands that the heat effect, which previously had been ascribed simply to heat of transition, should not occur at a single definite temperature, but should be observable over a marked interval. The observations actually agree with this demand. The "transition point" measured by thermal methods is never sharp, and the ferromagnetic properties do not disappear suddenly but gradually. The theory has even been confirmed quantitatively, for it is possible to calculate an approximately correct value for the heat effect from purely magnetic data.

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[1] * Definite evidence that such maxima in the boiling-point curves do not correspond to chemical compounds follows from the fact that by changing the pressure the composition of the mixture at the maximum can also be changed.

[2] TAMMANN, G., "Lehrbuch der Metallographie," p. 380, Leipzig and Hamburg.

166. Relation between Equilibrium and the Degree of Division of the Individual Phases.—It has been frequently stated that the phase rule can be applied only to systems in equilibrium, *i.e.*, stable systems. However, a phase is really stable only when it is not too finely divided but occupies a continuous space with the smallest possible ratio of surface to mass. As long as this condition is not satisfied, the surface tension, which is effective in solids as well as liquids, tends to reduce this ratio for a phase as much as possible and the system continues to change. In other words, stable equilibrium is not yet attained. An example of this is the familiar phenomenon that a difficultly soluble substance can frequently be precipitated in an exceedingly finely divided state, and after a time become coarse-grained, *i.e.*, larger individual crystals grow while smaller ones disappear. Since it cannot be assumed that the solid, crystalline substances, of which such precipitates are composed, can grow together directly, it must be assumed that the material is transferred from the smaller to the larger crystals by means of the solution phase. Obviously, this is possible only if the smaller crystals are more soluble than the larger. It can actually be proved experimentally that below a certain limiting size the solubility increases as the crystals become smaller. Hulett (1901) found that the solubility of $BaSO_4$ was 2.3 *mg./l.* for particles of 1.8μ and upwards in diameter, and 4.15 *mg./l.* for those of 0.1μ. For the same reason that finely divided precipitates have greater solubility, very small liquid droplets have greater vapor pressure.

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[1] * *J. Iron Steel Inst.*, p. 315 (1921).

Thus, whenever it is possible to retain matter in the labile state of very fine division for a long time,[1] the two phases of a one-component system, such as a liquid and its vapor, will not be in equilibrium at a definite pressure for a given temperature, as the phase rule requires, but the apparent equilibrium pressure depends upon the fineness of the division. Particles which are essentially unstable exist for very long periods in solid solutions; the solubility of the particles in these solid solutions is therefore greater than corresponds to a stable equilibrium, provided they be sufficiently small. This phenomenon is important in some metallographic processes (formation of osmondite in the annealing of steel), since by increasing the solubility of a substance in a metal the other properties can be decidedly influenced.[1]

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[1] These conditions are exceedingly important in the preparation and stability of certain colloidal sols (suspensoids). It is first required that the substance be very difficultly soluble in the liquid in order that the large particles should not grow at the expense of the smaller by means of material transferred through the liquid. Further, the particles must be prevented from touching each other, since otherwise they will form loose aggregates and precipitate, this can frequently be done when the particles assume electrical charge of the same sign and thus repel each other. As long as the charges are retained, the particles in the solution are stable and may remain so for a considerable period.

167. Adsorption.[2]—It has been mentioned previously that the boundary between liquid and gas is probably not discontinuous but that a sort of transition layer exists. This would mean that just under its surface a liquid has a slightly lower density and, correspondingly, the gas just above the liquid surface has a slightly greater density than "normal." Strictly speaking, the two phases bounding each other are not completely homogeneous, but density variations exist in the immediate vicinity of the interface. This effect is by no means limited to phases of the same substance; on the contrary, it is in these cases where it can only be shown indirectly.

Far more remarkable are the variations in the density of a gas or of a dissolved substance at the surface of a foreign solid substance; these are usually called **adsorption.** Theoretically, adsorption, *i.e.*, a density variation, is established at every boundary surface between two phases. It may be negative as well as positive, but at the surface of solids and liquids the adsorption of a gas is positive without exception. For dissolved substances it is sometimes, but rather seldom, negative. The amount adsorbed on 1 *cm.*^{2} is usually exceedingly small and appreciable effects are observed only when the surface area of the adsorbing substance is very large *i.e.*, it must be naturally porous or be prepared as a very fine powder. On account of its extraordinarily large surface, carbon of organic origin (wood or blood charcoal) has a remarkably high adsorption power for gases as well as for dissolved substances.

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[1] * For further information on this point see the article by C. Desch, "Colloid Chemistry," *Brit. Assoc. Repts.*, No. 4, p. 33 (1922), which includes a bibliography.

[2] This subject, although exceedingly important in industry and biology, includes such a wealth of detail that only a few of the fundamental viewpoints can be considered here. An exhaustive discussion is given by H. Freundlich in his book, "Kapillarchemie," 3rd ed., Leipzig (1924). * Briefer discussions may be found in Bogue, "Colloidal Behavior," vol. 1, p. 181 *et seq.* (McGraw-Hill Book Company, Inc. (1924)) and Bancroft, "Applied Colloid Chemistry," chaps. 1–3 (McGraw Hill Book Co, Inc. (1921)).

As the result of positive adsorption effects, a certain amount of substance is withdrawn from the gas or solution and is held on the surface of the adsorbing substance, the amount usually depending upon the concentration of the gas or solute remaining, and further to a high degree upon the temperature An equilibrium is actually established between the amount of adsorbed substance and the concentration remaining in the gas space or solution. This equilibrium may be established from higher as well as lower pressures and thus has a reversible character. Some of these adsorption equilibria have been exhaustively studied, one of them being the adsorption of CO_2 by charcoal The curves (**adsorption isotherms**) showing the relation between the gas pressure and the amount of gas adsorbed per gram of charcoal at various temperatures are represented in Fig. 48. At the higher temperatures the curves are straight lines at the beginning, but later bend toward the temperature axis. At high gas pressures the adsorbed amount increases less rapidly upon further

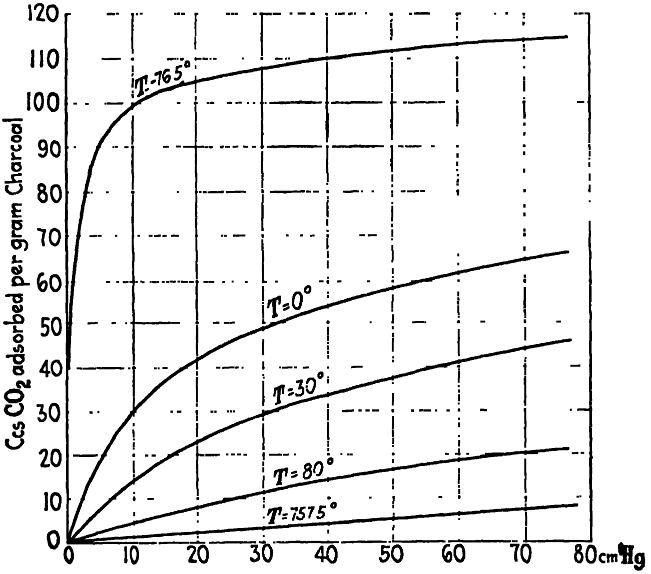

Fig 48

increasing the pressure, which means that the *adsorbent*, or rather its surface, approaches a state of saturation. The lower the temperature the sooner is the state of saturation reached. Even at −77°C. the adsorption effect is so great for CO_2, that practically all the gas is adsorbed on the charcoal if the gas volume per gram of charcoal is less than 80 *cc.* Air at −190° behaves the same as CO_2 at −77°, so that this phenomenon offers a very convenient method for making a space almost absolutely free from gas (Dewar).

The adsorption isotherms for solutions show qualitatively the same behavior as gases. Of the various empirical formulas which are suitable for expressing the experimental results, only the following one given by H. Freundlich will be mentioned;

$$y = \beta c^{\alpha},$$

in which y is the amount of substance adsorbed by a unit weight of the adsorbent, c is the concentration of the solution with which it is in equilibrium, α is a constant proper fraction, and β another constant.[1]

In many cases the adsorption acquires an irreversible character,[2] which is shown by the impossibility of removing the adsorbed substance by reducing the pressure of the gas or the concentration of the solution. An example of this is the adsorption of oxygen by platinum, investigated by Langmuir. In this case the gas was so firmly attached to the metal that it could not be removed by evacuation but only by chemical means (combination with H_2).

Quite frequently the directly observed adsorption process consists of a combination of several individual processes. An example of this is the process of dyeing. In the first moment of bringing together the dyestuff and the fabric, a reversible adsorption is clearly involved, from which it follows that a portion of the dye can be again washed out. After a time, however, it becomes so firmly attached to the fiber that it cannot be washed out and thus assumes the character of an irreversible adsorption.

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[1] * In the logarithmic form $\log y = \log \beta + \alpha \log c$, this equation is particularly convenient, since it then has the linear form of Eq (2) and both constants can easily be determined graphically.

[2] However, this is not meant to imply that the process is *theoretically* irreversible, but only practically so.

That electrical phenomena are involved in the adsorption of electrolytes is not surprising. For example, if an adsorbent is able to adsorb one ion of a solution more than the other, then the adsorbent must be electrically charged with respect to the solution. In the adsorption of electrolyte sometimes an exchange of individual constituents occurs in which the adsorbed ion gradually goes into chemical combination with the adsorbent, at the same time setting free another ion. This phenomenon is called "exchange adsorption."[1]

b. THERMODYNAMIC RELATIONS

168. The Phase Rule as a Result of the Second Law.—The Second Law requires that, for a liquid to be in equilibrium with its vapor, the latter must have a certain vapor pressure variable only with the temperature. In the same way it defines the more general equilibrium conditions between two phases by Eq. (162), for in this case also a perpetual motion of the second class would be conceivable if the concentration of a substance in one phase did not correspond to an absolutely definite concentration of the same substance in the other phase. The method of consideration is exactly the same as that in **124.** When solutions are involved, osmotic pressure may be used instead of vapor pressure. Since Gibbs' phase rule is based chiefly upon Eq. (162), it is frequently represented as a result of the Second Law.[2]

169. Special Thermodynamic Relations for the Equilibrium of Polycomponent Systems.—The extreme variety of equilibrium phenomena in systems of several components, of which the above examples give only an incomplete picture, indicates that this field is governed by no general relationships common to all its phenomena except that of the phase rule itself. Therefore the application of thermodynamics is limited to a number of special cases.

1. *Change of Solubility with Increasing Pressure.*—Between the equilibrium pressure, temperature, and heat of transformation, the Clapeyron-Clausius equation holds also for systems of several components, and the derivation of it can be expanded to this more general case.

As an example of the application of this equation to such a case, the temperature change of the solubility equilibrium with increasing pressure may be considered, a case which is closely related to the change of melting point with pressure. In general, the solubility of a substance, *i.e.*, the concentration c_0 in its saturated solution, is a function of pressure and temperature, thus

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[1] * See BARTELL and MILLER, *J. Am. Chem. Soc.*, **44**, 1866 (1922), **45**, 1106 (1923).

[2] * The derivation of the phase rule by means of the chemical potential (see **27**) is given in LEWIS, W. McC., *loc. cit.*, vol. 2, p. 264, and MACDOUGALL, *loc. cit.*, p. 148.

$$dc_0 = \frac{\partial c_0}{\partial p}dp + \frac{\partial c_0}{\partial T}dT$$

For the curve of constant solubility $dc_0 = 0$ and therefore

$$\frac{dp}{dT} = -\frac{\frac{\partial c_0}{\partial T}}{\frac{\partial c_0}{\partial p}}. \tag{166}$$

On the other hand, the Clapeyron-Clausius equation states that

$$\frac{dp}{dT} = \frac{\Lambda}{T(v_2 - v_1)}, \tag{167}$$

in which for the present case $\frac{dp}{dT}$ is the temperature-pressure change in which the solubility equilibrium is *not* displaced, Λ is the heat required to dissolve 1 mole of the solid substance in the *nearly saturated* solution, $v_2 - v_1$ is the volume change of the system in the solution process. By combining Eqs. (166) and (167) the result is

$$\frac{\partial c_0}{\partial p} = -\frac{\partial c_0}{\partial T}\frac{T(v_2 - v_1)}{\Lambda}. \tag{168}$$

As a rule, $v_2 - v_1$ is negative (the volume decreases), Λ and $\frac{\partial c_0}{\partial T}$ are positive. The equation thus states that $\frac{dc_0}{dp}$ in this case is positive, which means that at constant temperature and increasing external pressure the solubility generally increases.[1]

2. *Relation between the Partial Pressure and the Composition of a Mixture.*—In a mixture of liquids of definite composition each component in the vapor space has a definite partial pressure (at equilibrium) $p_1, p_2, \ldots$, the sum of which is the total pressure when the presence of non-condensible gases is excluded. While thermodynamically nothing can be stated at the beginning concerning the isothermal relation between the total pressure

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[1] * For the relation between temperature and solubility, see **145**.

and the composition of the mixture, a differential equation between the partial pressure and the composition has been derived by Duhem and Margules from the Second Law. For the special case of a two-component system, this equation takes the form

$$N_1 \frac{d\, ln\, p_1}{dN_1} + (1 - N_1)\frac{d\, ln\, p_2}{dN_1} = 0, \qquad (169)$$

where $N_1 = \frac{n_1}{n_1 + n_2}$ is the ratio of the number of moles of the one component to the total number of moles.[1] Thus, if the relation between one of the partial pressures and N_1 is known, then, with the help of the Duhem-Margules equation, after performing an integration for every value of N, p_2, and therefore the total pressure $p = p_1 + p_2$, can be found. The whole equilibrium of isothermal evaporation is thus thermodynamically determined by the behavior of a *single* p, N_1-curve.

170. The Abnormal Vapor Pressure of Small Drops.—As Lord Kelvin (1871) first demonstrated, small drops must have a higher vapor pressure than an extended surface, the difference depending chiefly upon the radius r of the drop and the surface tension σ

Suppose the droplet has a density δ and volume $\frac{4\pi r^3}{3}$, its mass therefore is $\frac{4\pi r^3 \delta}{3}$ If the radius of the droplet increases by dr, the mass increases $dm = 4\pi r^2 \delta dr$. The surface of the droplet is $4\pi r^2$, and, if the radius increases dr, the increase of the surface do must be

$$do = 8\pi r dr = \frac{2}{r\delta} dm.$$

If the surface decreases, then the surface tension does work amounting to

$$dA = \sigma do = \frac{2\sigma}{r\delta} dm$$

Now if the particles of radius r have the vapor pressure p, and those with radius $r - dr$ a vapor pressure $p' = p + \Delta p$, then for particles to grow by means of isothermal distillation the work performed per mole is (compare Eq. (78*a*))

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[1] A short and relatively simple proof of this equation was given by G. N. Lewis, *J. Am. Chem. Soc.*, **28**, 569 (1906), see also Lewis and Randall, *ibid.*, **43**, 235 (1921).

$$A' = RT\ln\frac{p'}{p} = RT\ln\left(1+\frac{p'-p}{p}\right) = RT\frac{\Delta p}{p}$$

and for a mass dm

$$dA' = \frac{RT\,dm\,\Delta p}{Mp}.$$

The Second Law now requires that dA and dA' be equal, and, therefore,

$$\frac{2\sigma}{r\delta} = \frac{RT}{M}\frac{\Delta p}{p} \qquad (172)[1]$$

Calculations according to this formula can give only approximate results, since for very small droplets σ is no longer constant, but must decrease with the radius of the drop

A numerical calculation according to this formula shows that a perceptible increase of vapor pressure is first to be expected when the droplets are exceedingly small For water droplets with radii of 10^{-5} *cm.* the vapor-pressure increase $\frac{\Delta p}{p}$ is only about 1 per cent

$$\frac{\Delta p}{p} = \frac{2\sigma M}{r\delta RT} = \frac{2\times 75\times 18}{10^{-5}\times 1\times 8.31\times 10^{7}\times 300} = 0.01.$$

However, very much smaller differences of vapor pressure are, of course, sufficient to cause a droplet to be unstable with respect to larger drops.

The relation between the solubility of very small particles and their radii (see **166**) is also given by Eq. (172) if the term p is considered as the osmotic pressure of the saturated solution. In this case, according to Eq (140), the saturation concentration can be directly substituted for p (Ostwald, 1900).

171. The Concentration of Dissolved Substances in the Surface Layer.—The surface tension of a liquid is usually changed when a substance is dissolved in the liquid, and it may now be shown that this change of surface tension must always involve concentration changes in the immediate vicinity of the surface. In order to obtain the relation, first derived by Gibbs, between these quantities, a cyclic process in four stages is necessary:

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[1] * Eqs 170 and 171 do not appear in the translation since they have been covered in **145**.

1. Dilute the solution with osmotic pressure Π, by the volume dv, keeping the surface constant. The work performed by the solution is, then,

$$dA_1 = \Pi dv.$$

2. Increase the surface of the solution by do, keeping the volume constant. Since σ in comparison with the original solution has changed by $\left(\frac{\partial\sigma}{\partial v}\right)_o dv$, and, further, since work has been performed against the surface tension, the work in stage 2 amounts to:

$$dA_2 = -\left\{\sigma + \left(\frac{\partial\sigma}{\partial v}\right)_o dv\right\} do$$

3. Concentrate the solution by decreasing the volume by an amount dv, again keeping the surface constant. Taking into consideration that the osmotic pressure may have changed in step 2, there results

$$dA_3 = -\left\{\Pi + \left(\frac{\partial\Pi}{\partial o}\right)_v do\right\} dv.$$

4. Decrease the surface at constant volume by an amount do, so that

$$dA_4 = \sigma do.$$

Once more, as the result of the Second Law, the total work performed over the entire cycle must be zero, and, therefore,

$$\left(\frac{\partial\sigma}{\partial v}\right)_o = -\left(\frac{\partial\pi}{\partial o}\right)_v \quad \text{or} \quad \left(\frac{\partial\sigma}{\partial c}\right)_o\left(\frac{\partial c}{\partial v}\right)_o = -\left(\frac{\partial\Pi}{\partial c}\right)_v\left(\frac{\partial c}{\partial o}\right)_v.$$

Now if $c = \frac{n}{v}$, it follows that

$$\left(\frac{\partial c}{\partial v}\right)_o = -\frac{n}{v^2} = -\frac{c^2}{n}$$

and, since $\Pi = cRT$

$$\left(\frac{\partial\Pi}{\partial c}\right)_v = RT,$$

from which follows

$$v\left(\frac{\partial c}{\partial o}\right)_v = \frac{c}{RT}\left(\frac{\partial\sigma}{\partial c}\right)_o.$$

But an increase of concentration $\left(\frac{\partial c}{\partial o}\right)_v$ inside the solution is only possible if some of the dissolved substance is removed from the surface layer. If the increase of surface is Δo, then a total of $v\left(\frac{\partial c}{\partial o}\right)_v \Delta o = -\Delta n$ moles must pass from the surface layer into the main body of the solution. The equation,

$$\frac{\Delta n}{\Delta o} = -v\left(\frac{\partial c}{\partial o}\right)_v = -\frac{c}{RT}\left(\frac{\partial \sigma}{\partial c}\right)_o, \qquad (173)$$

thus states that if the surface tension increases with increasing concentration $\left(\frac{\partial \sigma}{\partial c}\text{ is positive}\right)$ then the concentration in the surface is less concentrated with respect to the dissolved substance than the remainder. The converse is also true.

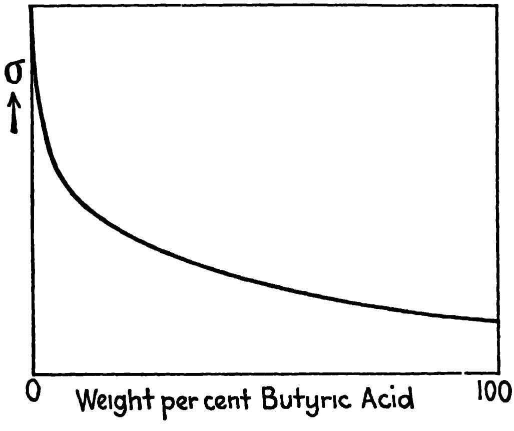

Fig. 49.

Now if a substance which increases the surface tension is added to a solution, the surface tension will change very little, since the surface layer contains less of the dissolved material than the main portion of the solution. The behavior is quite the opposite if the added substance lowers the surface tension, for in this case a very slight amount can serve to give a considerable concentration in the surface layer and an almost abrupt change in the surface tension may develop. A typical example of the effect of an added substance on the surface tension of a liquid is given by Fig. 49 for a complete series of mixtures of butyric acid and water. The increase of the surface tension of butyric acid by the addition of water is very slight, but a small amount of butyric acid lowers the surface tension of water very considerably.

Since increase or decrease of the concentration of the added substance in the surface layer is one of the characteristics of adsorption phenomena, Eq (173) is important as a thermodynamic connecting link between these phenomena and those of surface tension.

c. KINETIC THEORY

172. Theories of Adsorption.—As the reason for all adsorption phenomena, the presence of some sort of forces between the adsorbing surface and the adsorbed molecules must be assumed However, it may be seen from the variety of adsorption phenomena, already discussed, that the nature of these forces in individual cases is by no means uniform. The only thing common in all of them seems to be that the effective range of these forces is very small; at the most, it is of the order of magnitude of molecular diameters. This follows from investigations by Langmuir,[1] in which by measuring the adsorption of a gas on the surfaces of known dimensions (glass, mica, platinum) it was possible to demonstrate that the adsorbed layer was only one molecule deep in reversible as well as in irreversible adsorption. It is very probable that this result can be generalized and thus applied to other substances, such as carbon, for which the effective surface cannot be exactly stated.

In the reversible adsorption of gases the adsorbed molecules are obviously held on the surface by rather weak forces, since they can be removed quite easily by reducing the pressure. It is noteworthy that a portion of the reversible adsorption phenomena are dependent mainly upon the physical and only to a small degree upon the chemical properties of the gas adsorbed For example, oxygen and argon are adsorbed approximately equally by charcoal, but hydrogen very much less, a result of its lower boiling point. From this it follows that the forces effective in this group of adsorption phenomena are predominantly physical in nature. It is no great step to draw a parallel between these forces and those noted as the cause of molecular attraction in pure homogeneous substances. A calculation[1] of the work performed in this sort of adsorption leads to values which in order of magnitude are in good agreement with the work required for separating the molecules of pure substances (heat of evaporation).

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[1] *J. Am. Chem. Soc.*, **39**, 1848 (1917); **40**, 1361 (1918).

In those adsorption phenomena which are distinguished by firmer attachment and which frequently have an irreversible character, specific chemical effects become much more prominent. In such cases the total structure of the adsorbed molecule apparently undergoes a sweeping change in many cases, so that the chemical properties are much affected. Quite often the "reactivity" of the adsorbed molecules is much greater than the normal. For example, oxygen adsorbed on platinum is much more reactive chemically than ordinary gaseous oxygen. With gases which are already fairly reactive, the reactivity becomes considerably increased by a reversible adsorption on carbon. Chlorine adsorbed on carbon reacts directly with H_2 to form HCl.

The more intimate nature of the forces responsible for the chemical sort of adsorption phenomena has scarcely yet been explained in spite of the abundance of experimental material The complex nature of the phenomena involved, for example, in the adsorption of dissolved organic molecules on charcoal, may be seen from recent investigations by O Ruffs,[2] which indicated that pure carbon must first be "activated" by treatment with certain gases (H_2O, CO_2, NH_3, SO_2) at high temperatures in order to be able to adsorb perceptible amounts of phenol from an aqueous solution.

d. APPLICATIONS

173. Thermal Analysis.—The melting diagrams of mixtures are so very different from each other (compare Figs. 40 to 45), depending upon the mutual behavior of the components, that, conversely, from an experimental determination of the melting diagram, valuable conclusions may be drawn concerning the constitution of the solidified system and of the process involved during cooling. The method used is called *thermal analysis* and consists in measuring the velocities of cooling of each of a series of mixtures made from the same components in different proportions. The cooling curves thus obtained are of various types, of which the most important are discussed in the following:

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[1] EUCKEN, A , *Verh. Deut. physik Gesell.*, **16**, 345 (1914), *Z. Elektrochem.*, **28**, 6 (1922).

[2] *Kolloid-Z.*, **27**, 225 (1923).

1. *Cooling of a Pure Substance.*—At the melting point of a substance, the cooling curve shows a well-defined "break" or *halt point*, since all the heat of crystallization is liberated at a definite temperature (Fig. 50, curve *a*. System Ag – Pb).

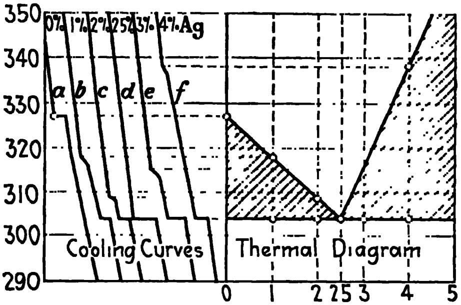

FIG 50

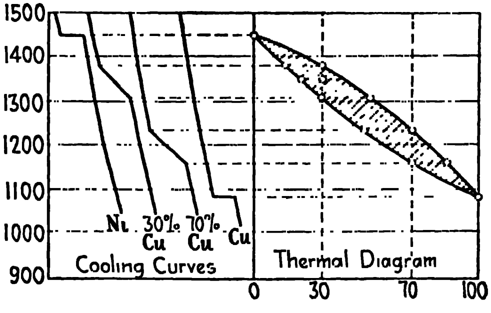

FIG 51

2. *Cooling of a Mixture from Which a Pure Component Crystallizes.*—At the beginning of crystallization the curve shows a break and, as a result of the heat liberated by crystallization, the rate of cooling is diminished. But since, by the freezing out of only one component, the liquid gets more and more concentrated with respect to those remaining, the melting point decreases continuously. Only at the eutectic point where all the remaining liquid solidifies does the temperature remain

constant for an appreciable length of time (Fig. 50, curves b and c).

3. *Cooling of a Eutectic Mixture.*—The whole liquid solidifies at one point and therefore shows a very decided halt point at the eutectic temperature (Fig. 50, curve d).

4. *Cooling a Mixture from Which a Solid Solution Separates.*—The beginning and the end of crystallization are indicated by breaks in the curve; a halt point does not occur (Fig. 51). Between the two breaks is a more or less large temperature interval over which the mixture solidifies.

The construction of the melting diagram from the breaks or halt points in the cooling curves is illustrated for the simplest cases by Figs. 50 and 51.[1]

174. Separation of the Constituents of a Liquid Mixture by Distillation.[2]—If a liquid mixture of about the composition A (Fig. 47a) is allowed to boil slowly and the vapor formed is removed continuously, then the remaining liquid becomes increasingly richer in the liquid with the higher boiling point, since the vapor always contains a larger fraction of the more easily vaporized component.[3] In other words, as the temperature of the boiling mixture increases, the straight line $A-B$ in Fig. 47a always moves toward the left until the point C is finally reached, where the liquid consists of the pure higher boiling component. But when the point C is reached, nearly all of the liquid has already been evaporated, so that the yield of the higher boiling constituent is vanishingly small. It will thus be seen that, while a certain separation of the two liquids is possible by means of such a method, it is either not complete or not efficient with respect to yield.

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[1] * It must be noted, however, that in a number of cases where the system is complicated by hidden maxima, etc., the thermal analysis is not sufficient to determine the composition of the compounds formed. Recently, the methods of X-ray analysis have been applied to such problems and new information obtained. See JETTE, PHRAGMÉN, and WESTGREN, *J. Iron Steel Inst.*, p. 193 (1924); WESTGREN and PHRAGMÉN, *ibid.*, p. 241 (1922).

[2] See also KUENEN, J. P., "Theorie der Verdampfung und Verflussigung von Gemischen," Leipzig (1906).

* YOUNG, SIDNEY, "Distillation Principles and Processes," The Macmillan Company (1922); and ROBINSON, "Elements of Fractional Distillation," McGraw-Hill Book Company, Inc. (1922).

[3] * Konowalow's rule.

The result is considerably better if the vapor is not immediately removed from the liquid but is conducted through a reflux condenser in which a fraction of it is condensed and, obviously, the higher boiling liquid is more easily condensed than the other. Thus, while the vapor passes through the condenser, the concentration of the lower boiling liquid in it always increases and, if the boiling is slow enough or the condensing surface is great enough, it is possible to obtain this constituent nearly pure The efficiency of the separation and yield of both the pure constituents obviously depends upon the length of time the boiling is continued and the efficiency of the condenser.

If a liquid mixture for which the boiling or condensation curve has a maximum (Fig. 47*b*) is subjected to reflux distillation, the residue from the the evaporation will not be either of the pure constituents but will have a composition corresponding to that of the maximum. Such residues are called **constant boiling mixtures.** By evaporating a dilute aqueous solution of HNO_3 under normal pressure, the most concentrated solution possible contains but 60 per cent of the acid.* Of course, in many cases the maxima on such curves shift when the pressure is changed. In the system $H_2O - HNO_3$ the maximum moves towards the higher concentration as the pressure is lowered, so that under low pressure a more concentrated solution may be obtained. If the boiling and condensation curves have a minimum, the vapor escaping from the condenser in the most favorable case has the composition of the minimum. Because the system water-ethyl alcohol has such a minimum at 95.6 per cent alcohol, it is not possible to obtain a greater concentration than 95.6 per cent alcohol by means of a simple distillation of a dilute solution

[1] * Carpenter and Babor, *Chem and Met Eng.:* **27** (1922), Babor, Dissertation, Columbia University, 1924.

SECTION C

CHEMICAL THERMODYNAMICS (INCLUDING ELECTROCHEMISTRY)

I. CHEMICAL EQUILIBRIUM

1. The Fundamental Laws in Detail

175. General Definition of Chemical Equilibrium.—The concept of *equilibrium* has its origin in mechanics. A pair of scales or a pendulum in the position of rest, even though either one is free to swing, is said to be in equilibrium. At first, it would appear that the characteristic of equilibrium is the invariance of the system with time—however, it may readily be seen that, while this characteristic is, indeed, essential, it is not sufficient for a complete definition. An arrested balance does not change its state with time, yet it cannot be described as being in equilibrium.

The criterion by which to determine whether a system is in equilibrium or not is expressed in the statement that the *potential energy is at a minimum.* This requirement is satisfied by the condition that the work performed dA (change of potential energy) must be equal to zero for an infinitesimal change. This, of course, also includes the case of the maximum of potential energy (labile equilibrium).

Equilibrium may be spoken of not only in mechanical systems, but also in chemical systems, *i.e.*, a number of substances which may react chemically with one another and form an isolated group in space—one may speak of *chemical equilibrium* in such a system.

Here the time invariance of the system is the prime characteristic for the equilibrium state, but, again, it is not sufficient to define the state. A chemical system in which no noticeable changes are taking place is not necessarily in equilibrium any more than is an arrested balance. At low temperatures most chemical systems are in a condition similar to an arrested balance and cannot be discussed from an equilibrium standpoint. A true chemical equilibrium, whose mechanical analogy is represented by a free swinging balance, requires a certain degree of mobility. Just as the free balance can be displaced by a small excess weight so must a genuine equilibrium state in a chemical system be chemically affected by trifling influences, such as the addition or the removal of small amounts of one or more of the substances involved in it. According to this, time invariance, associated with mobility, must be regarded as the criterion for true chemical equilibrium.

However, this characteristic which is so valuable in numerous cases cannot be regarded as completely satisfactory in all respects. A chemical system, under certain conditions, could be in equilibrium in spite of its "immobility," just as a balance beam could, by chance, be in equilibrium in its arrested position. In order to obtain a criterion of equilibrium which is universal, we must turn again to the thermodynamic condition of equilibrium discussed in **30**, that $A_{T,v}$ or $A_{T,p} = 0$, which is closely related to the condition for mechanical equilibrium; namely, that $dA = 0$, and forms the basis for the thermodynamic treatment of chemical equilibria (see **203** *et seq.*).

Meanwhile, for the empirical treatment of chemical equilibria it may be assumed that the chemical system is mobile in the above sense, so that the time invariance of the system may be considered as the equilibrium condition. For simplicity, it will always be assumed in what follows that a uniform temperature prevails in a given chemical system in the state of equilibrium.

a. Homogeneous Systems

α. GENERAL

176. The Incompleteness of Homogeneous Chemical Reactions.—In the first place, those chemical systems will be discussed which consist of a single homogeneous phase, and hence are designated as homogeneous chemical systems. This group primarily involves gaseous systems and solutions, yet homogeneous solid phases may also be considered, even though the appearance of an equilibrium is often markedly delayed.

According to the older conceptions of chemistry, every reaction, such as a combustion, proceeded to a complete interchange of the initial substances. Meanwhile the development of chemistry has shown that this viewpoint is not, in general, correct. The exchange of initial substances in a homogeneous reaction never goes so far that all are completely used up, but, instead, *the reaction always stops before all the initial materials have been converted*—hence, in the condition of chemical equilibrium all the reacting substances are present in greater or less proportion.

The reaction between hydrogen and sulfur vapor at about 400°C, where a considerable percentage of hydrogen sulfide is formed, serves for the qualitative demonstration of this proposition That the formation of hydrogen sulfide has not proceeded quantitatively can be established by analysis of the gas mixture. Still clearer proof of the incomplete formation as well as the partial decomposition into hydrogen and sulfur vapor consists in heating hydrogen sulfide to about 400°C, whereupon sulfur is deposited.

Examples in which a reaction stops exactly at or nearly at the point of half conversion of the initial substances are certainly not very frequent, for, as a rule, the equilibrium lies more to one side or the other for which either the initial substances or end products are in great excess, but never, even in the most violent reactions, such as explosions, do the molecules unite completely. In the explosion of oxyhydrogen gas a fraction, about 0.5×10^{-25} per cent, remains uncombined at room temperature. Though this may appear minute, it is nevertheless important for many phenomena and may even be determined by indirect measurement.[1]

To indicate that the more or less intermediate position of equilibrium can be attained from both sides, as, for example, a sulfur-hydrogen equilibrium from a hydrogen-sulfur vapor mixture on the one hand or from hydrogen sulfide on the other, it is expedient to write:

$$2H_2 + S_2 \rightleftarrows 2H_2S$$

instead of

$$2H_2 + S_2 = 2H_2S.$$

177. The Law of Mass Action (L.M.A.).—The position of a chemical equilibrium, that is, the degree of completion of the reaction in one or the other direction, is by no means fixed by the reacting materials, but depends upon the proportion of the ingredients involved. This proposition was first stated by Berthollet (1801), but it remained for the Norwegian investigators Guldberg and Waage (1867) to formulate it quantitatively. Their law of chemical mass action, abbreviated in what follows as **L.M.A.**, was exhaustively established on thermodynamic grounds by van't Hoff in 1877. It forms the basis of the experimental as well as the theoretical treatment of chemical equilibrium. Continuing with the analogy between chemical and mechanical equilibria, then the L.M.A. plays the same rôle in a chemical equilibrium that the lever law does in a mechanical process.

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[1] See, for example, **217**.

In the law of mass action the concentrations of the reacting participants appear as variables, and, as previously, we shall reckon with molar concentrations; *i.e.*, moles per liter. In order to distinguish easily and clearly between the concentrations of the different substances, it is often desirable to put the chemical symbols in brackets in place of the notation c used previously For example, $[H_2O]$ means the **molar concentration** of water as vapor or in solution. It is frequently of advantage in gas reactions to introduce the partial pressures of the substances from the gas laws $\left(c = \frac{n}{v} = \frac{p}{RT}\right)$ instead of concentrations.

178. Formulation of the L.M.A.—The L.M A. has the simplest form when we consider a pure (gaseous or dissolved) substance A for which no chemical reaction is proceeding. In this case the equilibrium is characterized by the trivial relation

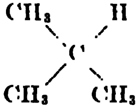
$$[A] = Const.$$

A more complicated case arises in the conversion of one molecular species into another (for example, through an internal rearrangement). If we write the reaction $A' \rightleftarrows A$, the L.M A. gives

$$\frac{[A]}{[A']} = Const.,$$

i e., the ratio of the concentration of both reacting substances is constant.

Such reactions occur with organic substances, whose molecules can exist in different isomeric forms, *i.e.*, they possess the same empirical formula but have a different constitution For example, butane has the empirical formula C_4H_{10}. The normal and isobutanes are respectively

$CH_3—CH_2—CH_2—CH_3$ and 

$$CH(CH_3)_3$$

Frequently, isomeric molecules are converted into one another so slowly that an equilibrium state is not reached. The grouping $—CO—CH_2—CO—$, however, changes relatively easily into the isomeric group $—C(OH) = CH — CO —$, so that a rapidly adjusted equilibrium is maintained between both isomeric species in substances containing these groups (*e g.*, aceto-acetic ester), a phenomenon which is designated as tautomerism

For a reaction of the type $A + B \rightleftharpoons AB$, we may consider the bromination of ethylene

$$C_2H_4 + Br_2 \rightleftharpoons C_2H_4Br_2$$

or the formation of phosphorus pentachloride

$$PCl_3 + Cl_2 \rightleftharpoons PCl_5.$$

Here the L M A gives

$$\frac{[AB]}{[A][B]} = Const \qquad (174a)$$

The common reaction

$$2A \rightleftharpoons A_2$$

belongs to the same class, when read to the right it is an *association*, when read to the left a *dissociation*. This reaction can also be written as

$$A + A \rightleftharpoons A_2,$$

which yields the expression

$$\frac{[A_2]}{[A][A]} = \frac{[A_2]}{[A]^2} = Const \qquad (174b)$$

The generalization of Eqs (174*a*) and (174*b*), *i.e.*, the erection of mass-action equations for any other reactions, such as

$$2H_2O \rightleftharpoons 2H_2 + O_2 \quad \text{or} \quad 2NH_3 \rightleftharpoons 3H_2 + N_2,$$

creates no further difficulties, for example, they are.

$$\frac{[H_2]^2[O_2]}{[H_2O]^2} = Const \quad \text{or} \quad \frac{[H_2]^3[N_2]}{[NH_3]^2} = Const$$

The L.M.A is described by the constant ratio of the products of the concentration of the components on one side divided by the product of the concentrations of the components of the other side The products are formed so that the concentration of every substance is used *n* times, if *n* molecules react or result in the reaction, *i e*, the concentration of a substance, of which *n* molecules react, enters in the L.M.A. in the *n*th power. For example in the equation

$$pC + qD \rightleftharpoons mA + nB$$

the L.M.A. has the form

$$\frac{[A]^m[B]^n}{[C]^p[D]^q} = Const. \qquad (175)$$

The preceding constants, designated by *Const.*, or in the future more simply as K, K_c, K_p, etc , are, in general, constant only at a given temperature, and vary with the temperature. For a fixed value of the constants K, etc the L M.A. is valid therefore only for a definite temperature.

In view of the fundamental significance of the L M A , it is necessary to illustrate its application in detail to the important homogeneous reactions occurring in gases and solutions.

β EQUILIBRIA IN GAS REACTIONS

179. Reactions Proceeding without Change in Mole Number. One of the simplest reactions for which the L.M.A. has been exhaustively investigated experimentally is the dissociation of hydrogen iodide [1]

$$2HI \rightleftarrows H_2 + I_2.$$

On introducing the L M.A

$$\frac{[H_2][I_2]}{[HI]^2} = K, \qquad (176)$$

and on substituting, in place of the concentrations, the partial pressures, $p_{H_2} = [H_2]RT$; $p_{I_2} = [I_2]RT$; $p_{HI} = [HI]RT$, we obtain

$$\frac{p_{H_2}p_{I_2}}{p^2_{HI}} = K. \qquad (176a)$$

In a similar way, we can substitute in place of the concentrations the number of moles, $n_{H_2} = [H_2]v$; $n_{I_2} = [I_2]v$; $n_{HI} = [HI]v$, so that

$$\frac{n_{H_2} \cdot n_{I_2}}{n^2_{HI}} = K. \qquad (176b)$$

The preceding case shows that the L.M A. retains not only its general form, but also the value of the constant unchanged whether we express the quantities of the reacting components by their concentrations, by their partial pressures, or by the number of moles.

It follows, then, that the equilibrium must be independent of the total volume in which the gas mixture is contained and also of the total pressure under which it exists. This result indicates that the volume v has been canceled out from the expression of the L M A. and that the equation holds for all reactions, which, like the hydrogen iodide equilibrium, possess the same number of molecules on the right and left sides of the equation. It appears, therefore, that the *equilibrium of all reactions which proceed without change in the number of molecules is independent of the total volume or total pressure.*

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[1] BODENSTEIN, M , *Z physik Chem.*, **22**, 1 (1897), **29**, 295 (1899).

The hydrogen iodide equilibrium was determined by Bodenstein by enclosing a known quantity of I_2 (a moles) and a known quantity of H_2 (b moles) in glass flasks. These were heated at the equilibrium temperature for a long time, and a known quantity of I_2 (x moles) reacted with an equal quantity of H_2 so that, according to the equation, a double quantity ($2x$ moles) of HI was formed. By rapid cooling it was possible to "freeze" the equilibrium, *i.e.*, to bring the mixture formed at higher temperature to a temperature range where the rate of change becomes vanishingly small. The number of moles of the individual components after the conversion amounts to $I_2 = (a - x)$; $H_2 = (b - x)$; $HI = 2x$, so that the L.M A. assumes the form

$$\frac{(a - x)(b - x)}{4x^2} = K. \qquad (176c)$$

The results obtained by Bodenstein at the boiling point of sulfur ($T' = 717°$) are reproduced in Table 28, in which the observed x values are placed next to those calculated from Eq. (176c) and the equilibrium constant $K = 0.01984$. The differences between the two are small and lie within the experimental

TABLE 28.—THE HI EQUILIBRIUM AT $T' = 717°$

a	b	$2x$	
		Calc	Obs
2.94	8.10	5.64	5.66
5.30	7.94	9.49	9.52
9.27	8.07	13.47	13.34
14.44	8.12	14.93	14.82
27.53	8.02	15.54	15.40
33.10	7.89	15.40	15.12

error. For small initial quantities (a) of I_2 the quantity of I_2 remaining ($a - x$) is very small, *i.e.*, the excess H_2 uses up almost the entire quantity of I_2. On the other hand, if the I_2 exists in considerable excess, then only a small part of it is combined, while nearly the entire H_2 is converted into HI.

Another example of a reaction of constant mole number, and one well investigated experimentally, is the water-gas reaction

$$CO_2 + H_2 \rightleftharpoons H_2O + CO,$$

whose equilibrium follows the relation

$$\frac{[H_2O][CO]}{[CO_2][H_2]} = K \tag{177}$$

The results of Hahn (1903) are given in Table 29. They were obtained by the use of the streaming method. In this method the initial mixture, which may consist of CO_2 and H_2, flows through a moderately wide tube into a bulb, from which the gas mixture escapes through a capillary. Since the gas remains in the bulb for a relatively long time, equilibrium is set up, if necessary the reaction can be accelerated by the use of a catalyst (see **237**), such as platinized asbestos. If the capillary is fine enough, the gas flows through so rapidly that it has practically the same composition when it reaches the cold portion as it had in the hot.

TABLE 29 WATER GAS EQUILIBRIUM AT T = 1259

Initial mixture, per cent		Final mixture, per cent			K	
CO_2	H_2	CO_2	$CO = H_2O$	H_2	Individual values	Average
10.1	89.9	0.70	9.46	80.38	1.591	1.602
		0.67	9.33	80.67	1.613	
30.1	69.9	7.18	23.00	46.82	1.581	1.575
		7.12	22.92	47.04	1.568	
49.1	51.9	21.52	27.83	22.82	1.576	1.603
		20.78	28.04	23.14	1.641	
		21.36	27.88	22.88	1.591	
60.9	39.1	34.67	26.28	12.77	1.557	1.601
		34.20	26.61	12.58	1.645	
70.3	29.7	47.66	22.79	6.76	1.613	1.599
		47.35	22.85	6.95	1.585	

Final average value, $K = 1.596$

180. Reactions Involving a Change in the Number of Moles.—The dissociation of nitrogen tetroxide to nitrogen dioxide may be discussed as an example of one of the few gas reactions, involving a change in the number of molecules whose equilibrium is rapidly established at room temperature.

$$N_2O_4 \rightleftharpoons 2NO_2.$$

The L.M.A. yields

$$\frac{[NO_2]^2}{[N_2O_4]} = K_c. \tag{178}$$

Let us represent the degree of dissociation by α, *i e.*, the fraction of the mole of N_2O_4 which is broken up into NO_2, and the number of undissociated moles of N_2O_4 existing originally by n_0. Then αn_0 moles are decomposed and there are only $n_0 - n_0\alpha = n_0\ (1 - \alpha)$ moles of N_2O_4 left over. The number of moles of NO_2 amounts to $2\alpha n_0$, two molecules of NO_2 arising from the one molecule of dissociated N_2O_4 The total number of moles n which are contained in a volume v amounts after dissociation, therefore, to

$$n = (1 - \alpha)n_0 + 2\alpha n_0 = (1 + \alpha)n_0.$$

The concentrations are

$$[NO_2] = \frac{2\alpha n_0}{v}$$

$$[N_2O_4] = \frac{(1 - \alpha)n_0}{v}$$

Hence from Eq. (178)

$$\frac{4\alpha^2 n_0}{v(1 - \alpha)} = \frac{4\alpha^2}{v_{M_0}(1 - \alpha)} = K_c, \tag{178a}$$

where $v_{M_0} = \frac{v}{n_0}$ represents the volume of the gas mixture, which includes a total of one mole of substance referred to the undissociated state (in the present case to 92 *g*. of N_2O_4).

If we introduce the partial pressures $p_{NO_2} = [NO_2]RT$; $p_{N_2O_4} = [N_2O_4]RT$ in Eq. (178) in place of concentrations, then

$$\frac{p^2_{NO_2}}{p_{N_2O_4}} = K_cRT = K_p, \tag{178b}$$

i.e., the L.M.A. retains the same form as in the application of concentrations, but the equilibrium constant assumes another value. This result may be generalized for any equilibrium.

The partial pressures may be substituted for the concentrations in every case, but the constants K_c and K_p are, in general, different.[1]

A relation between the total pressure p and the degree of dissociation α, which is often more convenient to use than the one between the partial pressures, is obtained from (178a) when the total volume v is replaced by the total pressure p according to the gas laws:

$$v = \frac{nRT}{p} = \frac{(1+\alpha)n_0RT}{p}. \tag{73c}$$

The final equation is

$$\frac{4\alpha^2 p}{1-\alpha^2} = K_cRT = K_p. \tag{178c}$$

The numerical value of K_p depends, of course, upon the units of measure chosen for p or for the partial pressures. In the following all data will be expressed in atmospheres as the unit of pressure.

Equation (178c) states that α decreases with increasing total pressure, and, in fact, for small values of α we have

$$\alpha \sim \frac{1}{\sqrt{p}}.$$

The number of moles $n = n_0(1 + \alpha)$ in all cases is smaller the greater the pressure, consequently the total pressure of the mixture is greater than with a pure gas. If α is eliminated from Eqs (178a) and (73c) instead of v, an equation of state valid for the mixture at constant temperature may be obtained in place of the Boyle-Mariotte law In order to obtain equations of state valid for a given temperature, the temperature relation between K_c and K_p must be known

In place of the degree of dissociation α it is often convenient to deal with the average molecular weight M_α of the gas mixture. M_α, obviously, varies in the preceding example between that of NO_2 (46), which is assumed for extremely small pressures, and that of N_2O_4 (92), which is reached at very high pressures, and we have

$$M_\alpha = \frac{g}{n} = \frac{g}{n_0(1+\alpha)},$$

---

[1] K_p and K_c differ by the factor $(RT)^{\Delta n}$ where Δn represents the excess number of moles of reaction products over reactants; *i. e.* $K_p = K_c\ (RT)^{\Delta n}$.

where g represents the weight of the mixture. On the other hand,

$$M_{N_2O_4} = \frac{g}{n_0},$$

hence

$$\frac{M_{N_2O_4}}{M_\alpha} = 1 + \alpha \quad \text{or} \quad \alpha = \frac{M_{N_2O_4} - M_\alpha}{M_\alpha}. \tag{179}$$

If we substitute this value for α in Eq. (178c), then

$$\frac{4p(M_{N_2O_4} - M_\alpha)^2}{(2M_\alpha - M_{N_2O_4})M_{N_2O_4}} = K_p. \tag{178d}$$

The gas laws in the form of Eq. (73c) may be applied for the experimental determination of α in reactions which involve a change in the number of moles, for here all values with the exception of α are relatively easy to obtain. Instead of relying upon Eq. (73c), we could go back to Eq. (73b), which yields the apparent molecular weight M_α from which α may likewise be obtained by means of Eq. (179).[1]

In the following table some numerical data on the dissociation of N_2O_4 are quoted from the investigations of Natanson[2] to illustrate Eq. (73c), (178c), and (178d).

TABLE 30. DISSOCIATION OF N_2O_4 AT $t = 49.7°C$.

1 p (*mm.*)	2 $\frac{v}{n_0}$ (*l.*)	3 $\frac{pv}{n_0}$	4 $\frac{K_p}{4}$	5 α obs.	6 α calc.	7 M_α obs.	8 M_α calc.
0	∞	(4020)			1.000		46.0
26.80	143.3	3840	129	0.910	0.917	48.2	48.0
93.75	382	3570	142	0.776	0.784	51.8	51.6
182.69	185.0	3380	157	0.680	0.673	54.8	55.0
261.37	124.5	3260	163	0.620	0.605	56.8	57.3
497.75	60.0	2990	153	0.485	0.483	62.1	62.0
∞		(2010)			0.00		92.0

---

[1] M. BODENSTEIN (*Z. Elektrochem.*, **16**, 961 (1910)) has described an apparatus, with which it is possible to estimate α in this fashion up to a temperature of about 1300°C., and with which the dissociation of the iodine molecule was tested.

[2] More recent investigations have been carried out by BODENSTEIN and BÖES (*Z. physik. Chem.*, **100**, 75 (1922)), which are less suitable, however, for proving the L.M.A.

The value $\frac{K_p}{4} = 0.197$ was used in the calculation of α and M_α in columns 6 and 8. The product $\frac{pv}{n_0}$, which would remain constant in a normal gas, decreases with increasing pressure in the ratio 2 to 1. The experimental error, which was kept within moderate limits, as a comparison of columns 5 and 6 as well as 7 and 8 shows, appears considerably magnified in terms of K_p, so that the variations in column 4 are of no significance

Ammonium chloride dissociates in the vapor state into ammonia and hydrogen chloride:

$$NH_4Cl \rightleftharpoons NH_3 + HCl.$$

The essential difference between this reaction and the N_2O_4 dissociation is that here the dissociation results in two different molecules whose concentrations in the gas mixture are equal only if they come from equimolecular quantities of the dissociation product or from pure NH_4Cl. Consider, now, the number of moles after dissociation from an initial quantity of N_0 moles of NH_4Cl:

For NH_4Cl: $n_0\,(1 - \alpha)$ moles.
For NH_3 : $n_0\,\alpha$ moles.
For HCl : $n_0\,\alpha$ moles

It follows from the L M A. that

$$\frac{\alpha^2 n_0}{v(1 - \alpha)} = \frac{\alpha^2}{v_{M_0}(1 - \alpha)} = K_c, \tag{180}$$

a formula which differs notably from Eq. (178*a*) by a factor 4. Similar to Eq. (178*c*) we obtain

$$\frac{\alpha^2 p}{1 - \alpha^2} = K_p. \tag{180a}$$

Let us add in addition an excess of n' moles of a dissociation product, say, of HCl vapor, to a gas mixture, resulting originally from n_0 moles of NH_4Cl, so that a certain displacement of the equilibrium takes place. If the degree of dissociation after the addition of this excess is designated by α', then the mole numbers possess the following values:

$$NH_4Cl = n_0(1 - \alpha')$$
$$NH_3 = n_0\,\alpha'$$
$$HCl = n_0\,\alpha' + n'$$

and we obtain

$$\frac{\alpha'^2 n_0\left(1 + \frac{n'}{n_0\alpha'}\right)}{v(1 - \alpha')} = K_c. \tag{180b}$$

By comparison of Eqs (180) and (180b) it is found that

$$\frac{\alpha'^2\left(1 + \frac{n'}{n_0\alpha'}\right)}{1 - \alpha'} = \frac{\alpha^2}{1 - \alpha}.$$

From this it follows that α must be greater than α' and the following conclusion is reached: *The degree of dissociation of a substance is always repressed by the addition of a dissociation product.*

An example which furnishes a beautiful qualitative demonstration of this law is the dissociation of the nearly colorless phosphorus pentabromide into colorless phosphorus tribromide and brown bromine vapor, which becomes noticeable at about 100°C. If phosphorus tribromide is added to the phosphorus pentabromide present originally, the degree of dissociation at 100°C. is so minute that a brown color is scarcely perceptible

The formation of water from oxyhydrogen gas,

$$2H_2 + O_2 \rightleftharpoons 2H_2O,$$

as well as the formation of CO_2 from carbon monoxide and oxygen,

$$2CO + O_2 \rightleftharpoons 2CO_2,$$

represents the dissociation reaction of water or carbon dioxide if read from right to left.

From $2n_0$ moles of water vapor (or CO_2) the mole numbers after dissociation amount to:

$$\begin{array}{ll} H_2O(CO_2) & : 2n_0\,(1 - \alpha) \\ H_2\quad (CO) & : 2n_0\alpha \\ \underline{O_2\quad (O_2)} & \underline{: n_0\alpha} \\ \text{Total } N & = n_0\,(2 + \alpha) \end{array}$$

The L.M.A for the dissociation then assumes the form (Eq. (174c))

$$\frac{n_0\alpha^3}{v(1 - \alpha)^2} = K_c, \tag{181}$$

or, if the total pressure,

$$p = \frac{n_0(2 + \alpha)RT}{a},$$

is substituted we get:

$$\frac{p\alpha^3}{(1-\alpha)^2(2+\alpha)} = K_cRT = K_p. \qquad (181a)$$

When α is very small, so that it can be disregarded, we obtain

$$\frac{p\alpha^3}{2} = K_cRT = K_p. \qquad (181b)$$

The influence of the excess of reaction products upon the dissociation of water and carbon dioxide is qualitatively the same, as in the example above. Here also, the addition of an excess of a reaction product always produces a repression of the dissociation.

The estimation of the degree of formation (x) is frequently of greater interest than the degree of dissociation of a substance. For example, according to the reaction for ammonia formation $3H_2 + N_2 \rightleftharpoons 2NH_3$ we can ask what fraction of the initial mixture has been transformed into ammonia at equilibrium from equivalent quantities of H_2 and N_2 (three moles H_2, one mole N_2).

Instead of this we can also investigate what fraction (x) of the gas mixture existing in equilibrium consists of NH_3 and of N_2 and H_2. Since the fraction in question is equal simply to the ratio of the partial pressure of ammonia to the total pressure, we have for the ammonia

$$x = \frac{p_{NH_3}}{p}$$

and for the sum of the partial pressures of N_2 and H_2

$$1 - x = \frac{p_{H_2} + p_{N_2}}{p},$$

and for the individual gases

$$N_2: \quad \frac{1-x}{4} = \frac{p_{N_2}}{p}$$

$$H_2: \quad \frac{3(1-x)}{4} = \frac{p_{H_2}}{p},$$

since $\frac{p_{N_2}}{p_{H_2}}$ must always be as 1 to 3.

Setting the up L.M.A. first for partial pressures, we obtain

$$\frac{p_{H_2}^3 p_{N_2}}{p^2_{NH_3}} = \frac{(1-x)^4 p^2 3^3}{x^2 \quad 4^4} = K_p = K_c(RT)^2. \qquad (182)$$

It can be recognized from Eq. (182) that the fraction of NH_3 formed should increase with increasing total pressure and it therefore forms the theoretical foundation for the **Haber process** of ammonia manufacture by which the small yield of ammonia at normal pressure is considerably increased by the application of higher pressure (*cf.* Table 31).

TABLE 31.—PER CENT OF AMMONIA FORMED AT DIFFERENT TEMPERATURES

T	$\log K_p$ (see Table 51)	$100r$			
		$p = 1$ *atm*	$p = 30$ *atm*	$p = 100$ *atm*	$p = 200$ *atm.*
773°	4.80	0.128	3.6	10.3	17.5
834°	5.33	0.069	2.5	6.0	11.2
904°	5.89	0.036	1.04	3.35	7.57
995°	6.45	0.019	0.57	1.85	2.90
1074°	6.91	0.011	0.35	1.17	2.38
1187°	7.43	0.007	0.20	0.67	1.30

181. Combination of Several Equilibria.—If at high temperatures carbon dioxide is added to the dissociated water vapor, which likewise exists in a dissociated state, both gases split off O_2; an equilibrium must accordingly be produced, so that the O_2 concentration of the dissociated water vapor is equal to that of the dissociated CO_2, *i.e.*,

$$[O_2] = \frac{K_{H_2O} \cdot [H_2O]^2}{[H_2]^2} = \frac{K_{CO_2}[CO_2]^2}{[CO]^2}.$$

Hence it follows that

$$\frac{[H_2O][CO]}{[CO_2][H_2]} = \sqrt{\frac{K_{CO_2}}{K_{H_2O}}} = K. \tag{183}$$

The resulting expression is none other than the L.M.A. valid for the water-gas reaction (Eq. (177)). We learn, therefore, that the constants for the water-gas equilibrium may be calculated from those of carbon dioxide and of water vapor. Experiments carried out by the streaming method yielded $\alpha = 1.41 \cdot 10^{-4}$ for the degree of dissociation at $T = 1396°$ and atmospheric pressure, and from Eq. (181*b*) $K_{CO_2} = 1.3 \cdot 10^{-14}$, and $K_{H_2O} = 0.25 \cdot 10^{-14}$, and, therefore, for the water-gas equilibrium

K is calculated to be 2.28, while from direct experiments a value in the neighborhood of 2.5 is obtained.

Other reactions may be resolved into simpler ones similar to the water-gas equilibrium. In all of these cases a simple relation analogous to Eq. (183) exists between the various constants of the L.M.A., so that the constant of the total reaction can be calculated from those of the partial reactions, or the constant of *one* partial reaction from those of the total reaction and the remaining partial reactions

As an example of such a case the **Deacon Process,** which was used for the preparation of Cl_2 from HCl, may be mentioned,

$$4HCl + O_2 = 2H_2O + 2Cl_2$$

The partial forms of these reactions are

the hydrogen chloride dissociation: $4HCl \rightleftarrows 2H_2 + 2Cl_2$,
and the formation of water vapor . $2H_2 + O_2 \rightleftarrows 2H_2O$,

from which the reaction equation of the Deacon process follows directly by addition, since the hydrogen given off is common to both reactions The equation to put in place of Eq. (183) becomes

$$K_D = \frac{K_{H_2O}}{K^2_{HCl}}, \tag{184}$$

where K_D is the constant for the Deacon process.

The equilibrium of the Deacon process reaches the midpoint between T = 700 and 1000°C, so that it can be measured relatively easily in this range by the streaming method. On the other hand, the equilibrium constants of the partial reactions are not accessible to direct measurement, owing to their minuteness. However, we are able to determine them through a thermodynamic relation (*cf.* **226**). We can use the equilibrium constant K_D found experimentally to test whether the equilibrium constants of the partial reactions obtained thermodynamically are correct. For[4] T = 1000° the thermodynamic values are: $K_{H_2O} = 10^{-19.86}$, $K_{HCl} = 10^{-10.38}$ from which $K_D = 10^{-0.84} \simeq 7.0$ from Eq. (184), while experiment yields $K_D \simeq 10$, which is a satisfactory agreement.

γ. SOLUTIONS (ELECTROLYTIC DISSOCIATION)

182. Historical.—Among the chemical equilibria, which are set up in solution and which have been exhaustively studied especially in aqueous solution, one group is particularly prominent; namely, equilibria formed by the dissociation of neutral molecules into constituents of opposite electrical charge, or ions. This phenomenon, called **electrolytic dissociation,** is of the greatest importance for the entire field of chemistry, because the characteristic common properties of many substances simply depend upon the fact that the same ion is dissociated.

For example, acids are distinguished in that they split off a positively charged hydrogen ion (H^+) and bases a negatively charged hydroxyl ion (OH^-). A compound acts stronger as an acid or as a base the more H^+ or OH^- ions its solution contains. In general, neutral salt solutions split off a positively charged metal atom, while the acid radical is negatively charged. This explains the well-known phenomenon that solutions of salts of any particular metal have numerous properties in common. Copper salt solutions are all colored blue, because they always yield a blue-colored Cu^{++} ion. Also the common precipitation reactions of salt solutions of a certain metal rest upon the same basis.

The theory of electrolytic dissociation was founded mainly upon the phenomena which one observes on electrolysis produced by the passage of an electrical current through a solution. The most important of the existing laws was discovered by Faraday (1833) and may be formulated as follows: when an electrical conductor suffers a chemical change at the electrodes by the passage of the current, the quantity of substance converted is proportional to the quantity of electricity which passes. Ninety-six thousand five hundred *coulombs* (ampère-seconds) always effects the conversion of a gram equivalent, *i.e.*, a mole of a univalent substance or $\frac{1}{n}$ parts of an n_e valent molecule or radical. The quantity of electricity, 96500 *coulombs*, is designated as the *electrochemical equivalent* or as 1 *Faraday* ($\mathfrak{F}$) For example, 1$\mathfrak{F}$ deposits 107.88 *g.* of univalent silver on the negative electrode (cathode) from a $AgNO_3$ solution, whereas $31.78 = {}^{63.57}\!/_{2}$ *g* of bivalent copper are deposited as metal from a copper sulfate solution. One $\mathfrak{F}$ forms 35.46 *g.* of chlorine at the positive electrode (anode) by the decomposition of hydrochloric acid, but only ${}^{16}\!/_{2} = 8$ *g.* of bivalent oxygen from the decomposition of water.

However, the electrolytic dissociation theory cannot be constructed from Faraday's law alone. Faraday himself explained his law on a purely chemical assumption. He imagined that the electric current acted first upon the solvent and that these decomposition products produced secondary chemical changes in the solution For example, according to Faraday, 1.008 *g* of hydrogen would first be deposited upon the cathode, and 8.00 *g* of oxygen upon the anode on the passage of $1\mathfrak{F}$ through an aqueous $CuSO_4$ solution between copper electrodes The hydrogen on the cathode would reduce the CuO in the $CuSO_4$ to Cu as a secondary reaction, so that metallic copper was precipitated, and at the anode the oxygen would oxidize the metallic copper to copper oxide, which unites with the residual SO_4 again to orm $CuSO_4$

Now if equal quantities of hydrogen and oxygen were always formed by he passage of $1\mathfrak{F}$ then Faraday's law simply reduces to Dalton's law of constant and multiple proportions.

An exhaustive test of processes in solutions, particularly of aqueous solutions, shows that Faraday's conception is not correct First, it has been shown that pure water conducts the current only very slightly, but that its conductivity increases the more salt is dissolved in it. Owing to this simple fact, the assumption that the water plays the primary rôle in the transport of the current must have aroused much hesitation

One of Hittorf's observations, namely, that changes proceed not only at the electrodes but also in the interior of the solution, speaks still more convincingly against Faraday's concept Hittorf showed that certain changes in concentration appear on passing a current through a solution This fact can be explained only by assuming that the particles of the dissolved salt migrate partly with and partly against the current Besides, one can follow these migrations during the passage of a current directly with the naked eye with colored salts, such as $KMnO_4$ From this, the qualitative conclusion follows that the dissolved salt and not the water accounts for the transport of electricity in the solution.

This gives an entirely different and more important meaning to Faraday's law than heretofore, which was clearly stated by Helmholtz in his Faraday lecture in 1881: *We must assume that every valence bond in an atom or radical involves a definite quantity of electricity, just as in the formation of a chemical compound several atoms or radicals are able to unite with one another* If matter possesses an atomic structure, then the same is true of electricity (*cf* **267**).

The conception that the dissolved salt and not the solvent accounts for the transport of electricity was developed quantitatively by means of a law discovered by Kohlrausch (1873), which may be formulated as follows: *The electrical conductivity of numerous electrolytes consists of two additive quantities characteristic of the ions of the electrolyte.* It is at present difficult to understand why the Kohlrausch law, which the discoverer himself had given the name "*law of the independent migration of the ions*," did not lead directly to the present-day ionic theory Indeed, it was believed that such a conception could not be reconciled with other facts, namely, that atoms firmly bound into molecules could separate spontaneously into ions when put in solution. In taking this position they overlooked the fact that there is a great difference whether a salt such as NaCl decomposes into neutral atoms or into charged ions. According to the modern viewpoint (**341** *et seq.*), the *important point in the union of Na and Cl to form NaCl does not consist in the formation of a neutral compound, but in the liberation of a negative charge by the Na atom and the absorption of the charge by the Cl atom*, thus, it is the exchange of an electrical charge between the two atoms which is important. When this occurs, *it is a matter of secondary importance whether the ions remain firmly bound to one another or are freely movable.*

The next assumption was that the ions were not always free but that the salt existed predominantly in the undissociated state, and that only very few ions appeared in the exchange from one salt molecule to another. From the standpoint of chemical equilibrium, such a conception (Clausius, 1857) signified an extremely small decomposition into ions The magnitude of the decomposition, however, in order to support the validity of the Kohlrausch law, must be about the same for all good conducting electrolytes.

In the course of time other fundamental phenomena were disclosed which favored a considerable electrolytic dissociation of dissolved salts and related substances. For example, Raoult in 1884 referred to the abnormal lowering of the freezing point (see **145**) which conducting substances showed.

Arrhenius (1887) was the first to announce without qualification the principle that all solutions which are good conductors of the electrical current are actually dissociated to a considerable degree instead of in minute traces. *If we disregard a number of qualitative arguments and the facts discovered by Hittorf and Kohlrausch, then the foundation of Arrhenius' ionic theory rests upon the quantitative calculation of the degree of dissociation by means of different methods* which will be outlined in the following paragraphs, and upon the agreement which these results show among themselves.

183. Methods for the Estimation of the Degree of Electrolytic Dissociation.—The definition of the concept of "degree of dissociation" (α) is the same for electrolytic dissociation as it is for gas reactions. We designate the fraction of the neutral molecules originally present which have dissociated into ions as the degree of dissociation. If the number of moles of neutral molecules *before* dissociation is n_0, then we obtain the following values for the number of moles *after* dissociation:

Undissociated molecules $n_u = n_0(1 - \alpha)$ (185)

Ions of one kind $n_i = n_0\alpha$

All ions $\sum n_i = 2n_0\alpha$; $3n_0\alpha$ respectively, where two, three or more ions are formed from a neutral molecule. The total number of neutral molecules and ions therefore amounts to:

$$n = n_0(1 + \alpha);\ \text{or}\ n_0(1 + 2\alpha),\ \text{etc.}$$

We are restricted exclusively to physical methods for the experimental determination of the degree of electrolytic dissociation in order to throw light upon the momentary state of the solution. The chemical methods of determination, frequently applicable to gas equilibria where one may "freeze" the equilibrium and establish the concentrations of the individual constituents analytically, do not apply, because the velocity with which an electrolytic equilibrium is established is exceedingly high even at the lowest temperatures which can be reached with liquid solutions.

The methods for estimating the degree of electrolytic dissociation may be classified into those which, in general, can also be applied to chemical equilibria with neutral dissociation products and those in which the electrical charge of the dissociation products plays a decisive rôle.

1. Of the former class, the methods introduced depend upon the application of the gas laws to solutions, and have already been discussed (see **149**). The estimation of the degree of dissociation α depends here, just as it did in Eq. (178c), upon the use of Eq. (73c), page 290, or Eq. (203), page 203, *i.e.*,

$$\Pi v = n_0(1 + \alpha)RT. \tag{73d}$$

Where the various values can be measured directly or indirectly (for example, the osmotic pressure Π by means of the freezing-point depression), the assumption that the gas laws are valid also for electrically charged particles (ions) is now, without doubt, strange. In fact, it may be demonstrated that the electrical charges of the ions give rise to another force besides that of osmotic pressure, therefore making a correction factor in the gas laws necessary, which, in general, cannot be neglected with strong electrolytes (*cf.* **188** *et seq.*). However, with the weak electrolytes this effect is so small that Eq. (73*d*) may be applied without change

2. In a number of cases some one constituent of the solution, such as the undissociated portion, or some ionic species, possesses

a characteristic physical property which serves as a quantitative measure by which the concentration c of the constituent may be estimated. We then obtain the degree of dissociation α by means of Eq. (185).

Foremost are the optical properties, for example, the rotation of the plane of polarization, the absorption of light for a definite color, etc If an ionic species is not itself colored, then the addition of another added substance to the solution still produces a color in many cases. In particular, the hydrogen-ion content may be easily determined, since a number of organic substances, the so-called *indicators*, are known whose color depends upon the hydrogen concentration * For the practical application of this method and method 5 following, the reader is referred to Mansfield Clark's "Determination of Hydrogen Ion Concentration" (2nd ed, Williams and Wilkins (1922)) (*cf* **191**).

3. A further method of attack depends upon the fact that the velocity of a reaction is proportional to the concentration of an ionic species.

Two cases must be distinguished: either the ionic species actually takes part in the reaction itself—for example, OH^- ion in ester saponification (see **232**)—or the ions act only catalytically—for example, the inversion of cane sugar by H^+ ions (see **237**). In both cases the determination of the concentration of the ions depends upon the measurement of the speed of reaction. The estimation of an unknown ionic concentration must, naturally, be preceded by a trial experiment with a known ionic concentration. For instance, in order to determine the OH^- content of an NH_4OH solution, a trial experiment with a KOH solution is first made, in which the OH^- concentration is approximately equal to the total concentration

The remaining methods for the determination of α depend upon characteristic properties, which depend directly upon the electrical charge of the ions, and therefore are not applicable to ordinary neutral chemical equilibria.

4. If an electric field is generated in a solution—for example, if an electrical potential is applied to the two electrodes in the solution—then a force $\mathfrak{K}$ is exerted upon the ions, which naturally possesses an opposite direction for the anions and the cations. By this action the ions undergo an acceleration, but they soon acquire a constant velocity as set forth in the principles in **14**:

$$v_0 = \frac{\mathfrak{K}}{f}. \tag{28a}$$

Now in electrical units the force $\mathfrak{K}$ is simply equal to the drop in potential per centimeter (see **21**) multiplied by the charge on a single ion $\frac{n_e\mathfrak{F}}{\mathbf{N}}$, *i.e.*,

$$\mathfrak{K} = \frac{n_e\mathfrak{F}\Delta E}{\mathbf{N}l},$$

where ΔE represents the difference in potential and l the distance between the electrodes.[1] If for this particular case we make $\frac{\Delta E}{l} = 1$ (drop of potential of 1 *volt/cm.*) and set $V_0 = U$, then

$$U = \frac{n_e\mathfrak{F}}{\mathbf{N}f}, \tag{186}$$

and, in general, we obtain

$$V_0 = \frac{U\mathbf{N}\mathfrak{K}}{n_e\mathfrak{F}} = U\frac{\Delta E}{l}. \tag{186a}$$

The quantity U, the velocity, which the ion assumes in a field of 1 *volt/cm.*, may be designated simply as the *migration velocity*. For highly colored ions the direct measurement[2] of the quantity V_0 in Eq. (186*a*), and therefore the determination of the migration velocity, occasions no difficulties. For example, the migration of the MnO_4^- ion can be followed with accuracy if a sharp boundary is formed between the solution of $KMnO_4$ and a solution of a colorless salt of similar ionic type, like KNO_3, of the same concentration and an equal potential drop is applied to the electrodes.

Since in a solution of a dissociated electrolyte the same number of positively and negatively charged ions must be always present, not only will one ionic species be shifted, such as the MnO_4^- ion, but the other ion, such as the positively charged K^+ ion, will migrate in the opposite direction towards the cathode. In the migration every gram-ion carries with it a definite quantity of electricity, according to Faraday's law, and, depending upon its valence, a whole number of electrochemical equivalents. As a result of this migration of the ions an electrical current flows through the solution, or, in other words, the solution acquires a certain electrical conductivity. The quantity of electricity flowing through the electrolyte may be determined in the following way.

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[1] This relation holds strictly only for the first instant after closing the circuit. If the current passes through the electrolytes for a longer time, changes occur in the solution and at the electrodes which occasion the production of other forces (**248** *et seq.*).

[2] *MacInnes and Smith, *J. Am. Chem. Soc.*, **45,** 2246 (1923) for improvements on this method.

If the cross-section of the electrolyte (assumed to be cylindrical) is q, then in 1 *sec.* $n^- = V_0^- q c_i$ moles of anion are shifted towards the anode; likewise $n^+ = V_0^+ q c_i$ moles of cation go toward the cathode, of which each mole carries $1\mathfrak{F}$ if they are univalent ions.

The effects of ions are additive in the transport of electricity, for, although the anion migrates against the potential gradient, it carries a charge opposite to that of the cation. The quantity of electricity I which flows through an electrolyte in 1 *sec.* is, therefore, equal to the sum of the quantities of electricity carried by both ions.

$$I = \mathfrak{F}(n^+ + n^-) = \mathfrak{F}(V_0^+ + V_0^-)c_i \cdot q = (U^+ + U^-)\mathfrak{F}c_i q \frac{\Delta E}{l}. \qquad (187)$$

Comparing this relation with Ohm's law, $\Delta E = IW$, the following expression for the resistance is obtained:

$$W = \frac{l}{\mathfrak{F}(U^+ + U^-)c_i q}. \qquad (188)$$

The resistance of a conductor 1 *cm.* long and 1 *cm.*^{2} in cross-section is designated as the **specific resistance** w, *i.e.*, $W = \frac{l}{q} w$, so that we have

$$w = \frac{1}{\mathfrak{F}(U^+ + U^-)c_i}. \qquad (188a)$$

In place of the specific resistance we deal more frequently in solutions with the reciprocal value, the **specific conductivity** κ:

$$\kappa = \frac{1}{w} = \mathfrak{F}(U^+ + U^-)c_i \qquad (189)$$

Now c_i represents the concentration of the anion as well as of the cation; therefore, according to Eq. (185),

$$c_i = \frac{n_i}{v} = \frac{n_0\alpha}{v} = c\alpha,$$

where c represents the total concentration of electrolytes, considered as undissociated (n_0 moles), which can be determined, by analysis. Therefore,

$$\kappa = \alpha\mathfrak{F}(U^+ + U^-)c. \tag{189a}$$

If $\frac{\kappa}{c} = \Lambda_c$ is substituted, then the usual concept of **equivalent conductivity** is obtained (so designated because $c = 1$). Then from Eq. (189a) a relationship is derived in which the concentration factor n_0 no longer appears explicitly:

$$\frac{\kappa}{c} = \Lambda_c = \alpha\mathfrak{F}(U^+ + U^-) \tag{190}$$

Now α and, therefore, Λ_c vary with the dilution and, qualitatively at least, it may be stated with assurance, even without defining the exact form of the L.M.A., that α always increases with dilution, and finally attains the limiting value of unity at infinite dilution. For infinite dilution, therefore,

$$\mathfrak{F}(U^+ + U^-) = \Lambda_\infty.^1 \tag{190a}$$

It will be seen that the law holds rigidly only for high dilutions; however, it may still be applied in lesser dilutions (Eq. (190)), if substances for which α has the same value at certain dilutions are compared. This is the case for most of the strong electrolytes (see **243**).

If it is assumed that the migration velocities U^+ and U^- are independent of the dilution, *i.e.*, possess the same value in Eqs. (190) and (190a), then they can be eliminated from both equations, resulting in

$$\alpha = \frac{\Lambda_c}{\Lambda_\infty}. \tag{191}$$

The degree of dissociation of a solution at a concentration c is given simply by the ratio of the equivalent conductivity at the concentration c to the equivalent conductivity at infinite dilution.

The following direct treatment likewise leads to this result. The conductivity must be proportional to the number of ions present and therefore also to the degree of dissociation α. The maximum value $\alpha = 1$ will be reached at infinite dilution, which corresponds to the conductivity Λ_∞. We have therefore the proportion $1:\alpha = \Lambda_\infty:\Lambda$, which is identical with Eq (191).

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[1] Equation (190a) represents the exact expression for the law of Kohlrausch which must of necessity follow from the ionic hypothesis.

It should be emphasized once more that the validity of the relation expressed in Eq. (191) depends upon whether and to what extent the hypothesis that U is independent of the concentration proves correct. To begin with, *its correctness is by no means assured*, for two oppositely charged ions cannot pass one another in a straight line without being affected, but they deflect one another from their paths, just as two approaching heavenly bodies cannot fly past one another in a straight line according to the law of gravitation. This *deflection effect* always disturbs the straight-line path of the ions and, therefore, results in a retardation of their motion in the direction of the electric field. The effect becomes the more apparent the closer the ions are to one another when they pass; from this it follows that the *migration velocity U must decrease with increase in concentration.* While this deflection effect is of considerable importance in numerous electrolytes (for example, neutral salts), in other cases, especially weakly ionized acids and bases, it becomes of less importance.

In cases in which the deflection effect is small, and therefore where U is practically independent of concentration, a certain difficulty arises in the application of Eq. (191) from the fact that the value of Λ_∞ cannot be obtained directly by experiment, but only by means of an extrapolation of the Λ_c values to infinite dilution (see **187**).

For the experimental estimation of Λ_c we go by means of Eq. (190) to κ and from this to the resistance w or W respectively. The latter may be determined with great precision, most simply by means of a Wheatstone bridge, for which a suitable alternating current is used, especially for electrolytes.[1]

5. The last method for the estimation of the degree of electrolytic dissociation depends upon the measurement of the electromotive force E of a concentration cell, for which the formula derived in **212** holds.

$$E = \frac{1.983 \cdot 10^{-4}\, T}{n_e} \log \frac{c_1}{c_2}$$

The importance of the method lies in the fact that it permits the measurement of an ionic concentration of any magnitude whatsoever if only the ionic concentration c_i is known. It therefore is able to give precise values for ionic concentrations which are so minute that all other methods fail to give reliable results.

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[1] * For the experimental precautions to be taken in this type of work, see Morgan and Lammert, *J. Am. Chem. Soc.*, **45**, 1692 (1923), and **46**, 1117 (1924).

184. Survey of the Degree of Dissociation of Various Aqueous Solutions.—The following table offers a survey of the electrolytic degree of dissociation α as it was determined for a number of substances according to the various methods. As far as the weakly dissociated substances (NH_4OH, CH_3COOH, $HgCl_2$) are concerned, the figures given may be considered as approximately correct, since the various methods enumerated above are applicable without much correction.

But it is just for these weakly dissociated substances (small α values) that many methods, such as osmotic pressure, give only approximate results. Bearing this in mind, then the concordance in α values, which are derived by the various methods, may be considered satisfactory and therefore, in the sense of what has been said in **182**, the theory of Arrhenius may be considered as proved experimentally for weak electrolytes.

The results obtained for strong electrolytes are less conclusive, since the majority of the methods of determination cannot yield any exact values for the degree of dissociation, owing to the mutual effect of the ions upon one another. As will be shown later, the true degrees of dissociation of the strong electrolytes are doubtless much larger than those α values given in Table 32. *While Arrhenius' hypothesis originally assumed only a considerable dissociation, in strong electrolytes, we are most likely concerned with nearly complete dissociation.*

185. Electrolytic Dissociation of Pure Solvents. Pure solvents are also dissociated to a certain extent into ions, but for substances which are liquid at ordinary and lower temperatures, the conductivity, and with that the degree of dissociation, are, in fact, extremely small.[1]

For example, the specific conductivity of pure water is $0.01 \cdot 10^{-6}$ at 0°, $0.04 \cdot 10^{-6}$ at 18°, $0.17 \cdot 10^{-6}$ at 50°; that of pure HCl approximately $0.2 \cdot 10^{-6}$ at −100°; of acetic acid, $0.04 . 10^{-6}$ at 18°; of pure ammonia,

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[1] It is worthy of note that this rule holds exclusively for substances for which separation of H^+ and OH^- or, perhaps, O^{--} ions occurs, but this is not true for metallic ions Most molten salts are excellent conductors of the electric current.

TABLE 32. THE DEGREE OF DISSOCIATION α OF VARIOUS SUBSTANCES IN AQUEOUS SOLUTION[1]

The Concentration of the Solution Amounts to about $\frac{1}{3}$ *Mole/l*, Except Where Other Values Given in Parentheses.

	Number of ions per molecule	Osmotic pressure: Isosmotic solutions (**142**)	Osmotic pressure: Freezing point	Specific effects **183** (2,3)	Electrical conductivity	Concentration cells
Cane sugar		0	0		0	
Ethyl alcohol			weakly associated		0	
Ammonia	2		0.02	0.005 (0.01)	0.008	
Acetic acid	2		weakly associated (0.5) 0.05 (0.01)	0.004 (0.5)	0.006 (0.5) 0.041 (0.01)	0.01 (0.25)
KCl	2	0.81	0.80		0.812	0.72
HCl	2		0.915 (0.1)	Abt 1	0.925 (0.1)	0.81 (0.1)
KOH	2		0.865 (0.1)	Abt 1	0.86 (0.1)	0.80 (0.1)
$SrCl_2$	3	0.84	0.80		0.78	
$K_4Fe(CN)_6$	5	0.52	0.48		0.52	
H_3PO_4	2 (See **192**)		0.29 (0.1)	0.25 (0.1)	0.28 (0.1)	

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[1]* It should be emphasized at this point that the (apparent) satisfactory agreement between the results of freezing-point and conductivity measurements of strong electrolytes given in practically every textbook on physical chemistry (also in Table 32) is somewhat illusory and, in fact, this apparent agreement has actually been misleading in that it has furnished a false support for the Arrhenius hypothesis of the existence of appreciable quantities of undissociated molecules of strong electrolytes. LEWIS and RANDALL (*J. Am. Chem. Soc.*, **43**, 1122 (1921)) have pointed out that this curious coincidence is due to an error made by almost all followers of the classical school who have applied the gas laws indiscriminately to ionic solutions, namely, in calculating the so-called degree of dissociation α by the relation $\alpha = \frac{(i - 1)}{(n - 1)}$, where i is van't Hoff's factor $\Pi_v = iRT$. A correct thermodynamic calculation leads to values of $(1 - \alpha')$ (See **188a**) which differ from the values of $(1 - \alpha)$ by 50 per cent. The values of $(1 - \alpha')$ so obtained, however, are in perfect accord, as they should be, with the results of other thermodynamic methods, such as *e.m.f.* measurements, but they differ by an appreciable amount even at high dilution from the conductivity values obtained from $\left(\alpha'' = \frac{\Lambda_v}{\Lambda_\infty}\right)$, this discrepancy is most evident when ions of high valence like those in $CuSO_4$ are employed. The reasons for this curious behavior will be more apparent after **188** *et seq.* have been considered. For more details regarding this point and the general question of the thermodynamic treatment of electrolytic solutions, consult LEWIS and RANDALL, *Thermodynamics* (*loc. cit.*), TAYLOR'S *Treatise on Physical Chemistry*, D. Van Nostrand and Co., New York, 1924, chap. XII, vol. 2, written by H. S. HARNED, particularly pp. 753 *et seq.*, and SCATCHARD, *J. Am. Chem. Soc.*, **47**, 648 (1925) where the most recent data obtained by the use of various thermodynamic methods have been critically reviewed and summarized.

$0.01 \cdot 10^{-6}$ at −75°, while an ordinary normal KCl solution possesses a conductivity of approximately 0.1 at room temperature. It is to be noted that the attainment of a degree of purity of liquids necessary for such conductivity measurements is accompanied by great experimental difficulties (exclusion of air, CO_2, etc.).

Every mixture of two such liquids increases the conductivity.[1] When plotted as a function of the composition, the conductivity must therefore pass through one or more maxima. In general, these lie considerably above the conductivity values of the pure substances. For example, the maximum conducting hydrochloric acid solution, about 6 normal, possesses a specific conductivity of 0.76 *mho*[2] (at 18°), which is approximately 10^7 times the values of the pure components.

The electrolytic dissociation of water is of considerable importance for numerous chemical reactions in aqueous solution. H^+ and OH^- ions are formed exclusively, that is, the dissociation goes according to the following scheme

$$H_2O \rightleftarrows H^+ + OH^-. \tag{192}$$

Presumably, O^{--} ions also exist in addition to OH^- ions, but only in very minute quantities. Since the degree of dissociation of water is very small, H^+ and OH^- ions unite almost completely as soon as appreciable quantities of these ions are brought together. A substance which is extensively dissociated in solution into H^+ and any anion was designated above as a strong acid. Likewise, a strong base is a substance which is almost completely dissociated into OH^- ions in solution.[3]

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[1] * KENDALL, J. (with BOOGE), *J. Am. Chem. Soc.*, **39**, 2323 (1917); (with GROSS), **43**, 1416, 1426 (1921).

[2] *Mho* = reciprocal ohms.

[3] * BRONSTED J. N. (*Rec. trav. chim. Pays-Bas*, **42**, 718 (1923); and *Z. physik. Chem.*, **108**, 192 (1924), with KAI PEDERSON) proposes to define an acid as a substance which *dissociates* H^+ and a base as a substance which *associates* H^+, according to the scheme:

$$\text{Base} + H^+ \rightleftarrows \text{Acid}.$$

Thus, OH^-, S^{--}, NH_3^0, and $C_2H_3O_2^-$ are bases, while $H_2PO_4^-$, HSO_4^-, Br^-, Cl^- are progressively very much weaker bases. In fact, Br^- and Cl^- do not show any tendency to combine chemically with H^+. NH_4^+ is a weak acid, but much stronger than H_2O and HS^-, which accounts for the effect of NH_4^+ on the $[H^+]$ of an NH_4OH solution. Similar conclusions hold for the substituted ammonias like aniline.

This definition of a base has certain advantages; it eliminates the hydration and subsequent dissociation of OH^- ions as the primary cause for the basic action of NH_3^0 and related substances; second, it appears to be in much

Therefore, if a strong base is neutralized by a strong acid, the reaction will always proceed in the direction from right to left,[1] while the anion of the acid and the cation of the base do not take part in the reaction, since they remain unchanged in the ionic state. For example, the neutralization of NaOH by HCl takes place according to the following scheme:

$$\underbrace{Na^+ + OH^-}_{NaOH} + \underbrace{H^+ + Cl^-}_{HCl} \rightarrow \underbrace{Na^+ + Cl^-}_{NaCl} + H_2O.$$

The correctness of the conception that the neutralization of all strong acids and bases is governed by the same reaction, namely, that represented by Eq. (192), finds support in the fact that the amounts of heat set free (change of heat content—see **199**) are the same in the neutralization of any strong acid by any strong base. The heat of neutralization of weaker, and therefore of incompletely dissociated, acids and bases shows values deviating from 13700 *cal.*, since the neutral molecules before neutralization must first dissociate, and therefore the heat of dissociation also enters into the measured heat of neutralization, in addition to the true heat of neutralization.

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better agreement with recent kinetic work on ion catalysis than is the older concept.

Bjerrum (*Z. physik. Chem.*, **104,** 147, (1923)) employs essentially the same view in discussing the basic dissociation constants of ampholytes like the amino acids and proteins. He is able to explain why the product of $k_a \cdot k_b$ for an ampholyte is always smaller than 10^{-14}, he also finds that amino acids at their isoelectric point, instead of existing as neutral molecules, exist almost entirely (> 99 per cent) as "Zwitter-ions" possessing the general formula

$$\overset{+}{NH_3} - R - \overset{-}{COO}, \text{ and not } NH_2 - R - COOH,$$

as has been usually supposed. (*Cf.* Bluh, *Z. physik. Chem.*, **106,** 341 (1923).)

This is a point of importance in the consideration of proteins as salts, as it means that the apparent dissociation constants of such ampholytes (k_a and k_b) are not the true acidic and basic dissociation constants (K_A and K_B), as has been generally considered, but are really the hydrolysis (*cf.* **193**) constants of the salt, *i.e.*,

$$K_A = \frac{K_W}{k_b} \text{ and } K_B = \frac{K_W}{k_a}$$

For a more general definition of acids and bases, see Lewis, G. N., "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., p. 142 (1923).

[1] According to Eq. (192)

TABLE 33.—HEAT OF NEUTRALIZATION OF STRONG ACIDS AND BASES

Acid and base	Heat of neutralization per mole
$HCl + NaOH$	13700
$HBr + NaOH$	13700
$HNO_3 + NaOH$	13700
$HIO_3 + NaOH$	13800
$HCl + LiOH$	13700
$HCl + KOH$	13700
$HCl + \frac{1}{2}Ba(OH)_2$	13800
$HCl + \frac{1}{2}Ca(OH)_2$	13900

The concentration of H^+ and OH^- ions in pure water or in exactly neutral solutions can be measured by various methods, the greater part of which have already been discussed in **183.** In place of the freezing-point method, which is inapplicable here, there is an indirect method, which will be described in **193.** For the determination of the values indicated in column 4, Table 34 (concentration cells), which depend upon the application of the law of mass action to the equation for the dissociation of water, see **191.**

TABLE 34.—CONCENTRATION OF H^+ AND OH^- IONS IN PURE WATER

1 Temperature	2 Method 2 (**183**)	3 Method 1 (**183**)	4 Method 5 (**183** and **212**)	5 Indirect method (**193**)	Probable value	6 K_{H_2O}
0°		0.31×10^{-7}	0.3×10^{-7}	0.3×10^{-7}	0.31×10^{-7}	$10^{-15.07}$
18°		0.78	0.85	0.7	0.78	$10^{-14.22}$
25°	1.2×10^{-7}	1.05	1.10	1.0	1.05	$10^{-13.96}$
50°		2.41	2.96	2.3	2.41	$10^{-13.22}$
100°		7.63	8.19	6.9	7.7	$10^{-12.23}$

The agreement of the results derived by the various methods is highly satisfactory, and may serve as further evidence for the reliability of the fundamental assumptions for the whole theory of dissociation.

186. Electrolytic Dissociation of Fused Salts.—A great number of liquids, most important of which are the molten metallic compounds, also exhibit a considerable conductivity in the pure state at higher temperatures. For example, the conductivity of molten $AgNO_3$ is 1.11 (300°); KCl, 1.91 (750°); $PbCl_2$, 2.4 (520°) —all measured in reciprocal ohms. A comparison of these figures with the conductivity values of good liquid conductors at room temperature shows that fused salts are without doubt highly dissociated.

In order to get a clear idea of the extent of dissociation of highly conducting fused salts, we must consider the molecular constitution of the solid crystalline state, which, theoretically, is not so very different from that of the melt. A salt crystal, according to **359**, consists in numerous cases of an ionic space lattice, and, in fact, the ions are so placed that a single ion, such as the K^+, is not bound to any one other ion, such as Cl^-, but is bound equally to all of its neighboring atoms. *Now such a crystal may be considered as completely dissociated just like its melt,* but it is to be noted, however, that this type of dissociation is different from the usual type, in which the dissociated particles are entirely free to move and are no longer bound by any force to the neighboring atoms; in fact, in the solid and liquid state the ions are occasionally unequally bound, *i.e.*, bound somewhat more to a single neighboring atom than to its other neighbors.

However, the case typified by gases in which a number of atoms and ions are united in the form of nearly rigid molecules, and are therefore bound exclusively on one side, may be classed as exceptions, especially those pure liquids which are distinguished by a high conductivity. *A sharp distinction is therefore lacking between the terms "bound into molecules" and "freely movable as ions," without which a clear conception of the idea of degree of dissociation is most difficult to grasp.* If the conception of the degree of dissociation is not firmly fixed in mind, naturally, every attempt to measure its magnitude by one of the classical methods is condemned from the start.

On the other hand, *with poorly conducting liquids* we have to assume that *the ions are predominantly united into ("rigid") neutral molecules,* which are complete in themselves. *Conse-*

quently, the concept "degree of dissociation" maintains its validity in such cases. However, the individual ion probably will only exist free for a very short time, since a continuous and rapid exchange of the ions presumably takes place between the molecules.

187. Application of the L.M.A. to Weak Electrolytes.—Weak electrolytes whose degrees of dissociation are relatively small, and for which the estimation of the degree of dissociation may be made by methods 1 and 4 of **183,** figure most prominently in the application of the L.M.A. to electrolytic dissociation. Nearly all organic acids and bases as well as certain inorganic acids and bases (such as NH_4OH) belong to this class. If we now consider a so-called binary, weak electrolyte, *i.e.*, a molecule which dissociates into only two ions according to the scheme

$$\text{Neutral molecule} \rightleftharpoons \text{cation} + \text{anion},$$

the L.M.A. takes the form:

$$\frac{[\text{cation}]\,[\text{anion}]}{[\text{neutral molecule}]} = Const.$$

If we introduce the degree of dissociation α and the volume v_{M_0} in which one molecule of substance considered as undissociated is dissolved, we have, exactly as in Eq. (180),

$$\frac{\alpha^2}{v_{M_0}(1 - \alpha)} = K.$$

Since in weak electrolytes α is generally determined by conductivity methods, it is convenient to introduce Λ_v and Λ_∞ by means of Eq. (191), so that we obtain[1]

$$\frac{\left(\frac{\Lambda_v}{\Lambda_\infty}\right)^2}{\left(1 - \frac{\Lambda_v}{\Lambda_\infty}\right)v} = \frac{\Lambda_v^2}{\Lambda_\infty(\Lambda_\infty - \Lambda_v)v} = K, \qquad (193)$$

a relation which is known as the **"Ostwald dilution law."**

Experience has shown this law to hold in numerous cases and it has always been excellently confirmed for weak electrolytes. As an example, two series of experiments with aqueous chloracetic acid and ammonium hydroxide will be offered.

[1] From now on v_{M_0} will be abbreviated to v for the sake of simplicity.

TABLE 35 [1]—APPLICATION OF THE OSTWALD DILUTION LAW TO AQUEOUS CHLORACETIC ACID SOLUTIONS[1]

$v = \frac{1}{c}$	$\Lambda_v \cdot 10^4$	α obs	α calc (aver $K = 156 \cdot 10^{-5}$)
20	51.6	0.166	0.163
205	132	0.423	0.43
408	170	0.547	0.543
2060	251	0.806	0.801
4080	274	0.881	0.88
10100	295	0.948	0.944
20700	300	0.963	0.971
∞	311	[1.00]	[1.00]

[1] From VAN'T HOFF and REICHER, *Z physik Chem*, **2**, 771 (1888)

TABLE 36 —APPLICATION OF THE OSTWALD DILUTION LAW TO AQUEOUS AMMONIA SOLUTIONS

v	$\Lambda_v \cdot 10^4$	$100\,\alpha$	$100\,K$
8	3.4	1.35	0.0023
16	4.8	1.88	0.0023
32	6.7	2.65	0.0023
64	9.5	3.76	0.0023
128	13.5	5.33	0.0023
256	18.2	7.54	0.0024

A practical difficulty arises in the application of the Ostwald dilution law, in that for weak electrolytes it is not easy to evaluate Λ_∞ accurately, since, for the high dilutions at which the substance is almost 100 per cent dissociated, conductivity measurements are, in general, no longer reliable. This difficulty is overcome by resolving Λ_∞ according to Eq (190*a*) into $\mathfrak{F}U^+$ and $\mathfrak{F}U^-$ and determining these values separately, and by using highly dissociated electrolytes (salts), where the extrapolation of the conductivities to infinite dilution involves a lesser error than with weakly dissociated substances.

For example, in order to obtain Λ_∞ for acetic acid, we estimate Λ_v for sodium acetate at various dilutions, from which we obtain by extrapolation a value Λ_∞, namely, 0.0785 at 18°C. Since, for the Na^+ ion the value $\mathfrak{F}U^+ = 0.0435$ may be accepted (Table 62), we obtain for the acetate ion: $\mathfrak{F}U^- = 0.035$. $\mathfrak{F}U^+$ for the hydrogen ion amounts to about 0.315 (this figure is probably only certain to one or two units in the last decimal place), so that for acetic acid Λ_∞ is 0.035 + 0.315 = 0.350. A really exact method for estimating Λ_∞ to about 0.1 per cent is at present still lacking.[1]

Frequently, we make use of an approximate rule due to Ostwald, applicable at least to organic acids of high atomic weights. According to this, the conductivity depends only upon the number n_a, which is the number of atoms contained in the acid, and, indeed, at 18° it gives an accuracy of ½ per cent:

$$\Lambda_\infty = 0.332 + \frac{0.140}{n_a} \quad (\text{for values of } n_a > 8).$$

The constant K of Eq. (193), which represents a direct measure for the degree of dissociation and therefore for the strength of an electrolyte, particularly of acids and bases, is frequently designated as the **affinity constant,** since at the same time it is an expression for the affinity of the hydrogen ion for the acid anion, or the hydroxyl ion for the basic cation (see **205**). Its magnitude has become of considerable importance in the investigation of chemical constitution, since certain changes (for example, substitutions) in an acid (or basic) radical produce very definite changes in the affinity constants.

Of the numerous regularities,[2] only the following will be emphasized. The acid character is strengthened and the basic character weakened by the introduction of aromatic radicals (for example, C_6H_5), hydroxyl groups, sulfur, halogens, carboxyl, nitril, and cyanides. The opposite effect is exercised by hydrocarbon, hydrogen, and amino groups. As an example the results for a number of substituted acetic acids may be considered.

	$K \cdot 10^4$
Acetic acid (CH_3CO_2H)	0.180
α-toluic acid ($CH_2(C_6H_5)CO_2H$)	0.556
Glycollic acid ($CH_2(OH)CO_2H$)	1.52
Thioacetic acid (CH_3COSH)	4.69
Monochloracetic acid (CH_2ClCO_2H)	15.6
Dichloracetic acid ($CHCl_2CO_2H$)	500
Trichloracetic acid (CCl_3CO_2H)	about 900
Cyanacetic acid ($CH_2(CN)CO_2H$)	37.0
Propionic acid ($CH_2CH_3CO_2H$)	0.134
Glycocoll ($CH_2(NH_2)CO_2H$)	Very small

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[1] For further details, see LORENZ, R., "Raumerfullung und Ionen beweglichkeit," Leipzig (1922). * Also, BATES, *J. Am. Chem. Soc.*, **35**, 519 (1913), and KRAUS, The Properties of Electrically Conducting Systems, Chemical Catalog Co., New York (1921).

[2] * For more details, see DERICK, *J. Am. Chem. Soc.*, **33**, 1174 (1911) and **34** (1912); HENRICHS, "Theories of Organic Chemistry," Translated by Johnson and Hahn, John Wiley & Son (1922). Also LA MER and BAKER, *J. Am. Chem. Soc.*, **44**, 1963 (1922), COHEN, GIBBS, and CLARK, *U. S. Pub. Health Repts.*, **39**, 401 (1924); and CONANT and FIESER, *J. Am. Chem. Soc.*, **46**, 1858 (1924), where the regularities have been extended to oxidation-reduction equilibria.

With isomers, the distance of the substituent from the place of the dissociation H^+ ion produces a marked influence upon the value of the affinity constants. For example, a radical in the ortho position to the hydrogen ion exercises a greater influence than one in the meta position. On the other hand, a radical in the para position sometimes has even an opposite effect to what it ordinarily has. As an example, the three isomers of hydroxybenzoic acid are given:

	$K \times 10^2$
Benzoic acid .	0 006
o-hydroxybenzoic acid	0 102
m-hydroxybenzoic acid	0 0087
p-hydroxybenzoic acid	0 0029

188a. State of Dissociation of Dissolved Neutral Salts.—An attempt to apply the L.M.A. to strong electrolytes, especially neutral salts,[1] would only be justified when the ionic concentration or the degree of dissociation is accurately known.

In fact, however, this is *not* the case, since the two most exact methods, namely, freezing-point and conductivity measurements, yield at best incorrect values; in the former, this results from an apparent diminution of the osmotic pressure caused by the electrical attractive forces which the ions exercise upon one another, in the latter as the result of the deflection effect discussed in **183**, 4 Since the latter is, likewise, a direct result of the electrostatic attraction of the ions, it is apparent that the correction to be applied to the equation $\alpha = \frac{\Lambda_v}{\Lambda_\infty}$ as result of the deflection effect must work in the same direction as the correction factor in the gas law.

It is strange, indeed, that the *apparent dissociation* α' which may be obtained directly from Eq (73*d*) (p 300) without any correction whatsoever, and the *second apparent degree of dissociation* α'' which is obtained directly from Eq. (191) *are in many cases very nearly the same* Table 37 serves as proof for this. In this table the apparent degree of dissociation α' obtained from freezing-point measurements for the salt (KCl), which has been thoroughly investigated, is compared with the α'' obtained by conductivity measurements, and at the same time shows the failure of the L.M.A. in its *direct* application.

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[1] By neutral salts those are meant which give no H^+ or OH^- on dissociation as the primary ions. Nevertheless, such a neutral salt may liberate $H^\cdot$ or OH^- from the solvent as a secondary action (**193**).

The striking agreement[1] of the numerical values for α' and α'', which for a long time sustained the erroneous assumption that α' and α'' represented the true dissociation, cannot be directly interpreted. What is intelligible is that there is a parallelism between them. As Kohlrausch pointed out, it is possible to reproduce empirically the relationship between the values α' or α'' and c at relatively high dilution by means of the formulas,

$$1 - \alpha' \sim \sqrt{c} \quad \text{and} \quad 1 - \alpha'' \sim \sqrt{c}.$$

TABLE 37 —APPARENT DEGREE OF DISSOCIATION OF KCl

Concentration	α' (freezing point)	α'' (conductivity)	$\alpha - \alpha'$ (Milner)	α	$\frac{\alpha'^2}{(1 - \alpha')v}$	$\frac{\alpha''^2}{(1 - \alpha'')v}$
0 005	0 960	0 956	0 038	0 998	0 115	0 104
0 01	0 940	0 942	0 053	0 993	0 147	0 153
0 02	0 915	0 923	0 074	0 989	0 197	0 221
0 05	0 882	0 891	0 115	0 997	0 335	0 364
0 10	0 856	0 862	0 162	1 018	0 509	0 538
0 20	0 824	0 831	0 224	1 048	0 771	0 817
0 3	0 802	0 810	0 27	1 08	0 975	1 034

Milner[2] was the first to attempt to calculate the difference between the true degree of dissociation α and α', in which he pointed out that only the electrostatic forces arising from the ionic charges act between the ions (see Table 37, column 4). For the true degree of dissociation one obtains values of α from α', which lie close to unity, *i.e.*, the strong electrolytes are almost completely dissociated (column 5).[3] Recently, P. Debye and

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[1] With other salts, for example, KNO_3, the agreement is, however, less striking.

[2] MILNER, *Phil. Mag* (6), **26**, 742 (1913).

[3] The viewpoint that the strong electrolytes are practically completely dissociated was first enunciated by N. Bjerrum (1909) and may now be considered as essentially established. (*Cf.* the reviews of L. EBERT, *Jahrb. Radioakt. Elektronik.*, **18**, 134 (1921) and F. AUERBACH, "*Ergebnisse der exakten Naturwissenschaften*," Bd. I, p. 228, Berlin (1922)).

E. Hückel have improved the theory of Milner in many respects, whereby the Kohlrausch $\sqrt{c}$ law results for dilute solutions (**188c**).

This result is in excellent accord with the considerations of **186** on molten salts, for, if the salts are practically completely ionized in the solid and liquid conditions, dilution and the further interposition of solvent molecules theoretically can produce no change; on the contrary, the degree of dissociation could only be increased by this means and under no circumstances could it decrease. It should be emphasized again that this state of dissociation of strong electrolytes, just as with molten salts, is quite different in principle from the state of dissociation of gaseous systems, or dissolved non-ionized molecules. In the former case, the dissociation products (ions) are bound to their neighbors by strong forces, which are predominantly electrical, so that the individual ion is hindered in its freedom of migration; in the other case the dissociation products migrate almost unhampered

Since the kinetic foundation of the L.M.A. (see **256**) depends upon the freedom of motion of the molecules, and its thermodynamic proof[1] upon the applicability of the simple gas laws, which, of course, is not permissible in this case, this treatment cannot be carried over to strong electrolytes as a matter of principle, even when the various degrees of dissociation, which differ but slightly from unity, are accurately known.

In spite of this, if we wish to adhere to the general form of the L.M.A. $\frac{c_1c_2}{c_u} = \frac{\alpha^2}{v(1-\alpha)} = K_c$, we can consider the mutual influence of the ions to be at a minimum when we substitute corrected values in place of the true degrees of dissociation α of c_1 and c_2, respectively. *These corrected values are often called the *relative activities of the ions.*

***188b. The Activity Coefficient as a Convenient Measure of Non-ideality.**[2]—For representing deviations from any ideal state, and particularly for those marked deviations which occur in the aqueous solutions of strong electrolytes, a number of workers in this field have found it very convenient to introduce a new thermodynamic concept called *the activity*,[1] which is related to the fugacity (see **142**) as concentration is to pressure; namely,

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[1] See **205**.

[2] * **188b, c, 191a,** and the starred portions of **191** and **196** have been added to the text by Victor K. LaMer.

$$\text{fugacity} = RT \cdot \text{activity}.$$

*Since the fugacity is nothing more than the vapor pressure corrected for all deviations from the gas laws, fugacity is simply an accurate measure of the tendency of a substance to escape from its surroundings. In an exactly similar way it may be said that the activity a is a quantity which accurately measures the escaping tendency of a substance expressed in concentration units for which corrections have been made for all deviations from the gas laws; *i.e.*, the absolute activity is equal to the concentration when the substance is a gas and obeys the gas laws; otherwise it is a *fictitious concentration* which would have to be employed in order to produce a given escaping tendency on the supposition that the ideal laws of gases were being obeyed.

*The particular advantage gained by the use of these quantities depends upon the fact that an equation of state of the form of the perfect gas law may be applied to any system regardless of whether the system is ideal or non-ideal or is in the gaseous, liquid, or solid state of aggregation.

*The result is that the differential equations of thermodynamics can be integrated, and relations like the law of mass action and its various corallaries obtained, whose forms are identical in all respects with those derived on the supposition that the gas laws are being obeyed, except that fugacity and activity now replace pressure and concentration in the various thermodynamic relations. When stated in terms of fugacities or activities the L.M.A. obviously has universal validity.

*The assumption that the *ideal* equation of state for liquids and solids will be of the same form as that for gases becomes very probable when the results of the equipartition principle are combined with the assumption that a constant and uniform environment prevails throughout the entire system, as was shown to be the case for dilute solutions in **150**.

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[1] *Introduced first by G. N. Lewis (*Proc. Am. Acad*, **43**, 259 (1907); *Z physik. Chem*, **61**, 129 (1907)) to replace the rather vague concept of active mass used by Guldberg and Waage.

*When the gas laws are valid (**45, 204**) the maximum work which one mole of substance *can perform* in expanding to infinite volume is given by

$$A_{T,p} = RT\ln c + Const. \tag{193a}$$

and by the same token the absolute activity of one mole of a pure substance may best be defined by the relation

$$A_{T,p} = RT\ln a + Const., \tag{193b}$$

where the constant of integration depends only upon the temperature chosen. The constant is equal to zero for the gaseous state, but has finite values when other states of aggregation are considered.

*When the substance considered exists in a state of solution — which implies nothing more than that it exists as a homogeneous mixture with other substances — it becomes necessary to replace $A_{T,p}$ by the differential quantity

$$\left(\frac{\partial A_{T,p}}{\partial n_1}\right)_{T,p,N_i=Const.} = \bar{A}_{T,p}.$$

* The negative value of this quantity $(-\bar{A}_{T,p})$, usually designated as the *chemical potential of the substance*, is called by G. N. Lewis the *partial molal free energy* $(\bar{F})$ of the substance. The decrease in the value of the function $\bar{F}$; namely $-\Delta\bar{F}$, represents the maximum work $(\Delta\bar{A}_{T,p})$ which the substance can yield in passing spontaneously from one state to another It is consequently a direct measure of the escaping tendency of the substance from a solution. In other words, $(-\bar{A}_{T,p})$ *represents the work which must be performed upon the system in order to transfer one mole of the substance to the attenuated gaseous state from a volume of solution so large that the process of removing one mole of substance does not change the composition* (N_1) *of the solution.* (*Cf.* **54** and **225.**)

* Thus the absolute activity of any substance can always be evaluated irrespective of whether it exists in the pure state or in a state of solution by determining the work necessary to convert the substance into the attenuated gaseous state where all environmental effects become zero and fugacity = pressure, and activity = concentration.

* The absolute activity has commonly no significance and, since experimentally it is difficult or often impossible with non-volatile

substances, to establish $\bar{A}_{T,p}$ for the conversion to the gaseous state, it is expedient to replace the absolute activity by the **relative activity** for which the standard state of reference is defined in terms either of the pure liquid or the pure solid state instead of the attenuated gaseous state. This is equivalent to setting arbitrarily both $\dot{A}_{T,p}$ and the integration constant equal to zero for the reference state; the activity in the new reference state accordingly becomes equal to unity. Hereafter, for simplicity, activity will always mean the relative activity[1] referred to a properly chosen standard state.

* The relation between the stoichiometric concentration c, which the chemist actually measures, and the activity concentration a, obtained from thermodynamic measurements, is given by the relation.

$$a = f \cdot c \qquad \text{or} \qquad f = \frac{a}{c}, \tag{193c}$$

where f is the **stoichiometric activity coefficient**[2]; f is defined by

$$\Delta\dot{A}_{T,p} = \dot{A}_{T,p} = RT \ln f, \tag{193d}$$

an equation which may be obtained by substituting Eq. (193*c*) in Eq. (193*b*) and subtracting Eq. (193*a*), $\bar{A}_{T,p}$ being set equal to zero for the state of reference, where the relative activity $a = c$.

* When a value of unity is obtained for f, it means that the substance obeys the gas laws; when its value deviates from unity, the extent of the deviation is a direct measure of the deviations which the substance exhibits from the ideal behavior exemplified by the gas laws. When f is greater than unity the system can perform work in passing to the ideal state.[3]

---

[1] * Whenever it is possible to determine the value of the integration constant, the relative values can, of course, be converted into the absolute values, but there is no practical necessity for doing this The question of the choice of the standard state is discussed by Lewis and Randall (*loc cit*, p 256). They give many graphic methods for the calculation of the activity from various types of data, so that here only a brief survey of this important branch of the subject will be given.

[2] * BRONSTED, *J Am Chem Soc*, **42**, 761 (1920).

[3] * There is a practical advantage in determining the escaping tendency in terms of a instead of $A_{T,p}$, since a can be made to approach zero, while $A_{T,p}$ always approaches $-\infty$ as the concentration approaches zero

* In studying solutions it is most convenient to define the standard state of the solute so that f approaches unity as a limit when the solute forms an infinitely dilute solution in each particular solvent, since all solutes obey the gas laws at infinite dilution regardless of the nature of the solvent.

* When the standard state of the solvent is taken as that of the pure solvent, the activity of the solvent may be termed the **osmotic concentration,** and its activity coefficient φ becomes the **osmotic coefficient.** For an electrolyte, φ is the same as van't Hoff's coefficient i divided by the number of ions composing the electrolyte (**185**). φ can be determined experimentally from the ratio of the observed osmotic pressure to that of the ideal osmotic pressure, *i.e.*,

$$\varphi = \frac{\Pi_{\text{obs}}}{\Pi_{\text{ideal}}}$$

Π_{ideal} should, of course, be calculated according to the general Eq. (145) given in terms of mole fractions, but the usual practice has been to consider Eq. (140) as the ideal law. The difference is of no significance in dilute solutions but in concentrated solutions φ when so calculated represents not only the departure from the gas laws but also the deviations due to Eq. (140) being an approximate form of Eq. (145). Since osmotic pressure measurements are difficult to perform, the osmotic pressure is more often calculated from measurements of the freezing-point or vapor-pressure depressions by equations like Eqs. (145*d*) or (144*c*) (pages 217 and 212).

* When the osmotic coefficient has been determined the activity coefficient of the solute can then be obtained through the relation

$$\frac{d\,ln\,f}{d\,ln\,c} = \frac{d\varphi}{d\,ln\,c} - (1 - \varphi) \qquad (193e)$$

by integrating the relation found between φ and c or, in case no simple relation can be found, by performing the integration of Eq. (193*e*) graphically.[1] Equation (193*e*) can be derived[2] from the Gibbs-Duhem equation connecting the chemical potentials or corrected vapor pressures of the solvent and solute; it is therefore thermodynamically exact. (Cf. **169.**)

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[1] * *Cf* LEWIS and RANDALL, *loc cit*

[2] * BJERRUM, *Z Elektrochem*, **24,** 325 (1918); *Z. physik. Chem*, **104,** 406 (1923).

* Fortunately, it is not always necessary to perform this laborious operation in order to obtain values of the activity coefficient of the solute, since the latter can be determined directly from vapor-pressure measurements, when the solute is sufficiently volatile, by the relation (*cf.* Eqs. (193*d*) and (213))

$$f = \frac{\text{vapor pressure (observed)}}{\text{vapor pressure (ideal)}}. \qquad (193f)$$

* The activity coefficients of electrolytes can be obtained from *e.m.f.* measurements on appropriate cells (**207** *et seq.*). *When contact potentials can be neglected, this method determines the activity coefficient of the individual ions by the relation*

$$f_{(\text{ion})} = \frac{\text{"concentration" measured by } e.m.f \text{ (Eqs. (219) } et\ seq.)}{\text{stoichiometric concentration}}. \qquad (193g)$$

* Solubility measurements, which are essentially vapor-pressure measurements into a solvent instead of a vacuum, furnish an exceedingly simple and accurate method for determining f for the saturating substance in liquid mixtures, and, further, this method can be used either for pure electrolytes and pure non-electrolytes, or for their mixtures.

* Since at equilibrium no work can be performed, it follows from Eq. (193*b*) that the activity of the solute in a saturated solution must always be equal to the activity of the solid solute. If now various foreign substances (either electrolytes or non-electrolytes) are added to a solution in equilibrium with a solid phase, the stoichiometric solubility (s) changes but the activity of the dissolved particles saturating the solution remains the same, *i.e.*,

$$f_0 s_0 = fs = f_1 s_1 = f_2 s_2, \text{ etc.} \qquad (193h)$$

* Letting the characters with subscripts 0 refer to pure water as solvent and those without subscripts refer to any solvent prepared by adding foreign substances to pure water, it follows that

$$\frac{f_0}{f} = \frac{s}{s_0} \quad \text{or} \quad -\log f = \log \frac{s}{s_0} - \log f_0. \qquad (193i)$$

The activity coefficient of the solute when saturating pure water can arbitrarily be set equal to unity, whence

$$-\log f = \log \frac{s}{s_0}, \qquad (193j)$$

but for purposes of comparing f with the f values of other solutes it is best to determine[1] $-\log f_0$ for each by plotting $\log \frac{s}{s_0}$ against some linear function of the total concentration and extrapolating to zero concentration. The extrapolated value of $\log \frac{s}{s_0}$ at zero concentration gives the value of $-\log f_0$; f_0 measures the deviations from the gas laws which the solute molecules exhibit in water, owing simply to the presence of other solute molecules at the concentration of a saturated solution. When the solute is highly insoluble $\log f_0$ is small and may often be neglected as in Eq. (193j).

* If the solute is an electrolyte and the solvent contains an ion in common with the solute, then $\sqrt[\nu]{K_{s\,p}}$ must be substituted for s in Eqs. (193h, i, j). Here ν is the total number of ions composing the solute whose activity coefficient is being measured and $K_{s\,p}$ is its solubility product (*cf.* **196**), or, what is the same thing,

$$\log a_{(\text{salt})} = \frac{\sum \nu_i \log a_i}{\nu} \tag{193k}$$

and

$$\log f_{(\text{salt})} = \frac{\sum \nu_i \log f_i}{\nu}, \tag{193k'}$$

since the activity of a salt is defined as the geometric mean of the activities of its ions, and $\nu = \sum \nu_i$.

* For example,

$$a_{\text{Ca}_3(\text{PO}_4)_2} = \sqrt[5]{a^3_{\text{Ca}} \cdot a^2_{\text{PO}_4}} \equiv$$
$$f_{\text{Ca}_3(\text{PO}_4)_2} = \sqrt[5]{f^3_{\text{Ca}} \cdot f^2_{\text{PO}_4}} \equiv$$

* When the solubility product is introduced in place of the solubility, the activity coefficient can be determined just as accurately theoretically in a solvent containing an ion in common (homoionic solvent) with that of the solute as for a solvent in which no common ion (heteroionic solvent) is present.

* **188c. The Theory of Debye and Hückel.**—The qualitative explanation given in (**188***a*) for the diminution of the osmotic pressures of the ions as well as the diminution in the mobility

of the ions due to interionic forces has been quantitatively developed by Debye and Hückel in some recent papers.[1]

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[1] * Bronsted and La Mer, *J. Am. Chem. Soc.*, **46**, 566 (1924).

* Although the fundamental assumptions are fairly simple, the papers are highly mathematical in character, owing to the general nature of their equations, and for this reason only an outline of their method will be sketched here. They express their results in terms of activity coefficients and employ the assumption of the complete dissociation of strong electrolytes. The fundamental idea underlying their treatment, as well as that of Milner, is that, owing to the electrical attractions,[2] an ion of a given sign will, on the average, be surrounded by more ions of unlike sign than by ions of like sign, so that, when the solution is diluted, the separation of the ions involves the performance of internal work, which results in an increase in the energy content of the solution. Debye and Huckel calculate this *internal electrical energy* U_e, originating from the unequal distribution of the ions, *considered first as point charges*, by a straightforward application of the Boltzmann principle of probability distribution (see **16, 34, 135**), which enables them to express the average density of electricity ρ in a unit of volume (1 *cm.*^{3}) of a solution in terms of the *average electric potential* ψ and the total number (n) of ions present; namely, for a uniunivalent electrolyte,

$$\rho = n\epsilon\left(e^{-\frac{\epsilon\psi}{kT}} - e^{+\frac{\epsilon\psi}{kT}}\right) \simeq -2n\epsilon\left(\frac{\epsilon\psi}{kT}\right). \qquad (193l)$$

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[1] * *Physik. Zeit.*, **24,** 185, and 334 (1923), see also **25,** 97 (1924), and particularly the review of the subject of strong electrolytes in which the theory is presented in a somewhat simpler form by E. HUCKEL, *Ergebnisse der exakten Naturwissenschaften*, **3,** 199 (1925).

* A. A. Noyes gives an excellent presentation of some of the fundamental principles of the theory in *J. Am. Chem. Soc.*, **46,** 1080 (1924). The reader will find his critique of considerable aid in studying the original papers. However, he did not discuss the important influence which ionic size plays at concentrations above 0.01 M as much as might be desired. The discrepancies between the theory and the data given in his table (page 1101) and his various curves at higher concentrations, but which he does not consider invalidate the theory, are due very largely if not entirely to the omission of this factor. This point is fully described in the original. (See pages 331–334 for further discussion and for references, also **191a.**)

[2] * It is assumed that the electrical forces involved obey Coulomb's law (Eq. (194)).

ϵ is the unit of electric charge, k and T have their usual significance.

*This equation may be derived as follows. Consider a fixed positive ion, say a K^+ ion in a KCl solution, and an element of volume dv in its neighborhood as sketched in Fig. 51*a*. If no interionic forces existed, the gas laws would apply to the solution, since an equal number of K^+ ions and Cl^- ions would enter and leave dv per unit of time, *i.e.*, there would be a random distribution. Interionic forces, however, exist, and as a consequence the work $+\epsilon\psi$ must be performed in order to bring a positive ion from infinity into dv. The ion thus acquires an additional potential energy $+\epsilon\psi$. A negative ion would acquire the potential energy $-\epsilon\psi$, thus losing potential energy.

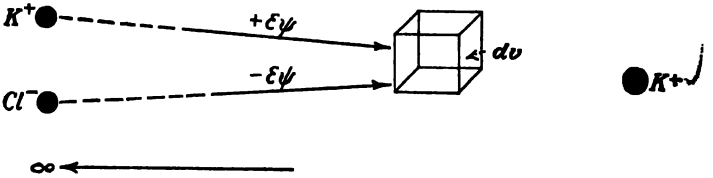

Fig 51*a*

*Now the Boltzman principle states that the ionic distribution is a function of the ratio of the electrical potential energy of each ion to its thermal energy kT, and is expressed as follows: on the average, there will be

$$n_+ = ne^{-\left(\frac{+\epsilon\psi}{kT}\right)}\,dv \text{ positive ions and}$$

$$n_- = ne^{-\left(\frac{-\epsilon\psi}{kT}\right)}\,dv \text{ negative ions}$$

present in dv.

*The change in the amount of electricity in dv with time, due to the presence of an excess of positive or negative electricity at any given moment, is shown schematically in Fig. 51*b*. The mean density of electricity with respect to time is negative, since more Cl^- ions enter dv than do K^+ ions, and quantitatively is equal to the sum of n_+ and n_-, each ion being multiplied by its respective charge $\pm\epsilon z$, which in the present case is $\pm\epsilon$, since the valence z equals ± 1.

* For an uniunivalent salt, on eliminating dv

$$\rho = +\epsilon n_+ + (-\epsilon n_-) = n\epsilon\left(e^{-\frac{\epsilon\psi}{kT}} - e^{+\frac{\epsilon\psi}{kT}}\right) \qquad (193m)$$

$$= -2n\epsilon \sin hyp\left(\frac{\epsilon\psi}{kT}\right), \qquad (193m')$$

which is equivalent to the last term in Eq. (193*l*), since $\left(\frac{\epsilon\psi}{kT}\right)$ is usually very small [1]

* Now the electric potential ψ and the density of electricity ρ are connected by the Poisson equation of electrostatics; namely,

$$\nabla^2\psi = \frac{d^2\psi}{dr^2} + \frac{2d\psi}{rdr} = \frac{-4\pi\rho}{D}, \qquad (193n)$$

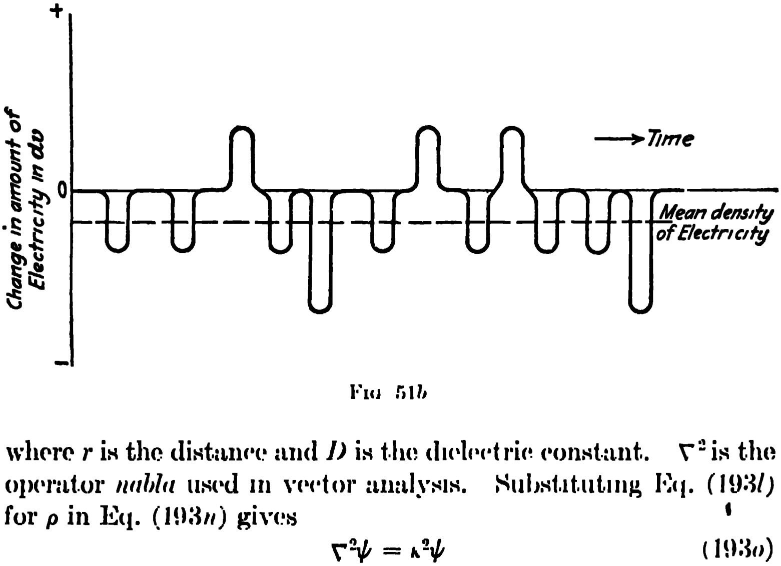

Fig 51*b*

where r is the distance and D is the dielectric constant. ∇^2 is the operator *nabla* used in vector analysis. Substituting Eq. (193*l*) for ρ in Eq. (193*n*) gives

$$\nabla^2\psi = \kappa^2\psi \qquad (193o)$$

---

[1] * The error introduced by this approximation is a minute one (*Cf.* MELLOR, *loc cit*, p 616) However, with salts of high unsymmetric valence type like $AlCl_3$, Eq (193*m*) does not necessarily equal Eq (193*m'*), since the even powers in the expansion of Eq (193*m*) do not cancel out as they do with symmetrical types like $MgSO_4$ or KCl. Bronsted has repeatedly called attention to the fact that the principle of the ionic strength (*vide infra*) breaks down even in highly dilute solution when applied to mixtures of salts of highly unsymmetric valence type. Unpublished calculations by the writer (V.K L) make it appear very probable that this curious anomaly will be explained by the use of an expanded form of Eq (193*m*) instead of Eq. (193*l*). (See also *J. Am. Chem. Soc.*, **46**, 558 (1924))

where

$$\kappa = \sqrt{\frac{8\pi n\epsilon^2}{DkT}} \qquad (193p)$$

and the differential equation can then be solved for ψ. κ is a most important quantity in this theory. $1/\kappa$ has the dimensions of a distance and by its use the introduction of an average distance between ions based upon the cube root of the concentration is avoided, a procedure employed by many previous investigators, notably Ghosh, in their attempts to solve the same problem. Debye and Hückel show that the use of an average distance leads to incorrect results since the ions in a solution are free to move and are not restricted to oscillating about fixed points as in crystal. $1/\kappa$ is therefore called the "characteristic or probability distance." This distance varies as the square root of the concentration and is of the order of the diameter of the ions at moderate concentrations.

*Physically, $1/\kappa$ measures the distance at which the potential of the ion considered has fallen to $1/e$ of its value owing to the presence of a surrounding atmosphere of other ions. This gives one way of defining the depth of the **Helmholtz double layer,** a concept of much importance in the study of colloid and electrode phenomena (**211**).

*When we consider the general case of a more complex electrolyte dissociating into the following numbers of ions per molecule:

$$\nu_1 \;.\; \quad \nu_i \;.\;.\; \quad \nu_s \text{ (total } = \nu),$$

and the numbers per cubic centimeter,

$$n_1 \;.\; \quad .\; n_i \quad .\;.\; n_s,$$

corresponding to ions of the sorts 1 i . s, and possessing the valences

$$z_1 \;.\;.\; \quad z_i \;.\; \quad .\; z_s$$

where z is a whole number either positive or negative, and these ions are in turn dissolved in a solvent containing various other ions having the numbers per cubic centimeter,

$$n_1 \;.\;.\;.\; n_i \;.\;.\;.\; n_s, \text{ (total for all ions } = N),$$

and the valences

$$z_1 \;.\;.\;.\; z_i \;.\; \quad .\; z_s,$$

Eqs (193*l*, *m*) must be replaced by similar but more general expressions. In the general case

$$\kappa = \sqrt{\frac{4\pi\epsilon^2}{DkT}\Sigma n_i z_i^2} \qquad (193p')$$

and finally

$$U_\epsilon = -\frac{\Sigma N_i z_i^2 \epsilon^2}{2D} \cdot \kappa. \qquad (193r)$$

Equation (193*r*) is an approximation valid only for highly dilute solutions. By introducing U_ϵ in any one of the thermodynamic functions (**28**), the chemical potential of the ions can then be evaluated and from this the deviations, which the ions exhibit from the gas laws due simply to interionic attractions, in terms of the osmotic coefficient of the solvent φ or in terms of the activity coefficient f of the solute for either an ion of the i^{th} sort or for the entire salt under consideration can be obtained, as described in **188b,** Eqs. (193*d*, *e*). This procedure gives:

$$(1 - \varphi)_{(\text{solvent})} = w\frac{\epsilon^2}{6DkT}\sqrt{\frac{4\pi\epsilon^2}{DkT} n\Sigma \nu_i} \qquad (193s')$$

$$-lnf_{(\text{ion})} = z_i^2 \frac{\epsilon^2}{2DkT}\sqrt{\frac{4\pi\epsilon^2}{DkT}\Sigma n_i z_i^2} \qquad (193t')$$

$$-lnf_{(\text{salt})} = \frac{\Sigma \nu_i z_i^2}{\Sigma \nu_i} \cdot \frac{\epsilon^2}{2DkT}\sqrt{\frac{4\pi\epsilon^2}{DkT}\Sigma n_i z_i^2} \qquad (193u')$$

where w is a valence factor equal to

$$\left(\frac{\Sigma \nu_i z_i^2}{\Sigma \nu_i}\right)^{3/2}$$

*From an empirical study of the data available in 1921, Lewis and Randall[1] were led to the formulation of a remarkably simple law; namely, *that in dilute solutions the activity coefficient of a given strong electrolyte is the same in all solutions of the same ionic strength.*

*They define the **ionic strength** μ as one-half of the sum of the stoichiometric molality of each ion multiplied by the square of the valence or charge. In the present notation this becomes equal to

$$\mu = \tfrac{1}{2}(m_1 z_1^2 + m_2 z_2^2 + m_3 z_3^2 + \ . \ . \ . \ ) = \tfrac{1}{2}\sum m_i z_i^2$$

if m_i is used as the molar concentration of an ion instead of its concentration in molecules per cubic centimeter. Theoretically, the ionic strength functions as a concentration unit which takes account of the changes in the electrical environment of a solution owing to a change in the number of ions present.

---

[1] **J. Am. Chem. Soc*, **43,** 1141 (1921).

*For the usual case of a salt composed of two kinds of ions, Bronsted and La Mer[1] reduced the equations of Debye and Huckel to simpler terms, yielding finally:

$$(1 - \varphi) = \alpha z_1 z_2 \sqrt{\mu} = 0.38_{(H_2O)} z_1 z_2 \sqrt{\mu}, \qquad (193s)$$

$$-log_{10} f_{(ion)} = \frac{3}{2.3} \alpha z_i^2 \sqrt{\mu} = 0.50_{(H_2O)} z_i^2 \sqrt{\mu}, \qquad (193t)$$

$$-log_{10} f_{(salt)} = \frac{3}{2.3} \alpha z_1 z_2 \sqrt{\mu} = 0.50_{(H_2O)} z_1 z_2 \sqrt{\mu}, \qquad (193u)$$

equations which they also showed could be obtained on empirical grounds involving primarily the introduction of the concept of ionic strength under certain restrictions. Here α is a *universal* constant depending only upon k, T, and D, the dielectric constant of the pure solvent. Using Drude's values for the dielectric constant of pure water, $\frac{3\alpha}{2.3}$ has the exact values of 0.485 (0°C.), 0.495 (15°C.), and 0.505 (25°C.); α is thus almost independent of the temperature. In Eqs. (193*s* and *u*) z_1 and z_2 refer to the valence of the cation and the anion of the salt.

*Equation (193*t*) states that the activity coefficient of an ion in a *highly dilute solution* depends only upon the square of its own valence and upon the square root of the ionic strength. This conclusion is in harmony with what one would expect on the basis of Coulomb's law, although the value of α cannot be derived directly from Eq. (194).

*Experimental verification for these equations is given in Fig. 51*c*, taken from the data of Bronsted and La Mer, which were obtained by measuring the increase in the solubility of certain difficultly soluble cobaltammine salts (s_0 = 0.00054 to 0.00005M), when various foreign neutral salts were added to the solution. Of the various methods (**188b**) which can be employed to evaluate the activity coefficients of electrolytes, the solubility method proves to be the most accurate when working at very low concentrations, since the freezing-point and *e.m.f.* methods commence to yield erratic results below 0.003 and 0.001M respectively.

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[1] * *J. Am. Chem. Soc.*, **46**, 555 (1924).

*The points plotted in Fig. 51*c* represent experimental values of $-\log f$ corresponding to the increase in the solubility ratio obtained with the solvent salts indicated in the legend and the heavy straight lines represent the theoretical values demanded by Eq. (193*u*) when $-\log f$ is plotted against $\sqrt{\mu}$.

*The data prove that at low concentrations: (1) The value of α as calculated by the theory of Debye and Huckel is correct

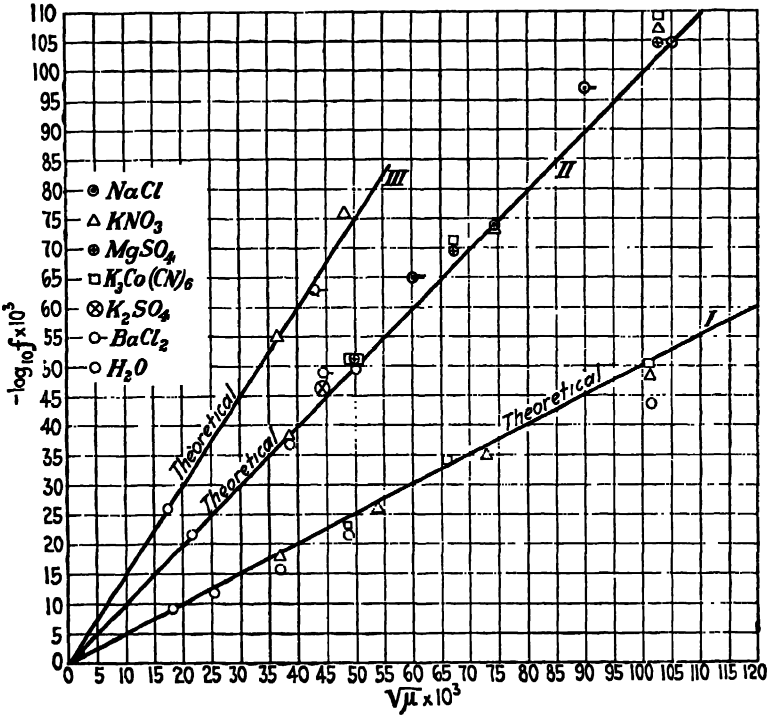

FIG 51*c*

within the limits of error for which D is known for pure water, since the slope of line I equals 0.50. (2) The valence factor z_1z_2 (z_i^2 for a single ion) is correct, since the slopes of the lines corresponding to the saturating salts of the types I(KCl), II($MgCl_2$ or Na_2SO_4), III ($AlCl_3$ or $K_3Fe(CN)_6$) are in the ratio of 1:2:3. (3) The principle of ionic strength is valid for the simpler types considered, since the values of f when compared for different solvent salts at the same ionic strength agree among themselves for a saturating salt of given valence type but do not agree when compared at the same molar or equivalent concentration, as was shown previously by Lewis and Randall.

*The theory as developed thus far deals only with the so-called *ideal salt* solution, where the properties of the solution depend simply upon the numbers and valences of the ions and do not involve the individual characteristics of the ions. The laws given above are consequently limiting laws whose validity increases with the dilution, and should be viewed in this light.[1] Allowing a deviation of 1 per cent in f, the region of ideal salt solutions extends to about 0.02μ, or for most uniunivalent electrolytes to 0.02M, though in certain cases, notably HCl, a deviation of this order occurs at 0.005M (*cf.* **149**).

*With rising concentration, the activity coefficient depends to an increasing degree upon the chemical character of the ions in the solution. The theory of salt solutions as developed by Bronsted and by Debye and Huckel takes account of these individual peculiarities by recognizing that *ions are not point charges but in a first approximation may be considered as rigid spheres of finite size.*

*It can be shown that this assumption results in Eqs. (193*t* to *u*) being multiplied by the factor $\frac{1}{1 + b\kappa}$, where b is the *average*

---

[1] * Randall and Vanselow (*J Am. Chem Soc*, **46**, 2418 (1924)) by improving the freezing-point technique have extended the existing data on HCl, TlCl, and $Pb(NO_3)_2$ to concentrations below 0.01M. They show that all salts of the same valence type do not have *exactly* the same activity coefficients up to 0.01μ, as Fig 51*c* also shows. This is not surprising, for the various effects of ionic size can vanish *completely* only at infinite dilution, a point which they do not consider. Unfortunately, the errors in the freezing-point method are so great below 0.003M—their values of the osmotic deviations $(1 - \varphi)$ vary by as much as 50 per cent below 0.003M—that the data have little bearing on the question at hand in this crucial range. On the other hand, their data appear to be very concordant above 0.005M, and fit Eq. (193*w*) just as closely as they do their empirical equation in which they vary the value of α. Scatchard (*J. Am. Chem. Soc*, **47**, 651 (1925) makes the same criticism of their interpretation and concludes "that at present, there are no experimental data which are not fitted within their experimental error by Eqs (193*v*, *w*) up to 0.01M and none on uni-univalent electrolytes, other than HCl, for which the equation does not hold up to 0.1M." (See **191a** for the other effects of ionic size)

effective diameter[1] *of the ions.* Now $\kappa = 0.33 \, 10^8\sqrt{\mu}$ and Eq. (193u) can, therefore, be expanded in ascending powers of $\mu^{1/2}$; yielding

$$-\log_{10} f_{(\text{salt})} = 0.50 z_1 z_2 \sqrt{\mu} - 1.7 \cdot 10^7 b z_1 z_2 \mu + $$
$$+ 5.5 \cdot 10^{14} b^2 z_1 z_2 \mu^{3/2} + \ . \ . \ . \qquad (193u'')$$

*When the solution is dilute the terms higher than the first become negligible, since b = about 10^{-8} *cm.*, and we are left with the ideal Eq. (193u) involving only the square-root term. In higher concentrations the second and third terms are no longer negligible and the activity coefficient depends more and more upon the size of the ion, primarily as a linear function of b (*cf.* Fig. 51g, p. 344).

*Bronsted proposed[2] the following equations, which he considers valid to approximately 0.1 to 0.2μ·

$$(1 - \varphi) = \alpha z_1 z_2 \sqrt{\mu} + \beta c \qquad (193v)$$

$$-\log_{10} f_{(\text{salt})} = \frac{3\alpha}{2.3} z_1 z_2 \sqrt{\mu} + \frac{2\beta}{2.3} c. \qquad (193w)$$

They may now be considered as first approximations of the complete theory. (Cf. Eq. (193y), **191a**).

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[1] *The physical significance of b is that of an average value for the distance up to which positive as well as negative ions can approach a given ion, the ions being considered as spheres of finite radius having their charges concentrated as points in the center, and the interior of the ion considered to have a dielectric constant D equal to that of the surrounding medium Accordingly b in the case of equally large positive and negative ions should be of the order of the sum of the two radii or the ionic diameter However this diameter must not necessarily always be the same as that of the true ion, since the ions presumably have a sheath of water molecules surrounding them, and b is accordingly only an approximation to reality It should also be noted that Debye and Huckel use the symbol a for our b. In their later papers they restrict the use of b to the radius of the ion

[2] *Originally (1921), only for uniunivalent electrolytes. Many data verifying the equations are given in *J Am. Chem Soc*, **44,** 938, 877 (1922); for biunivalent electrolytes, *ibid*, **45,** 2898 (1923). It should be noted that with mixtures of higher-valence types the concentration unit of the β term becomes more complicated, as it is composed of a part depending upon μ and a part depending upon the molar or equivalent concentration.

The factor 3 in the first term and the factor 2 in the second term of Eq. (193w) follows from Eq. (193v) if one applies the thermodynamic equation (Eq. (193e)) correlating the osmotic and activity coefficients.

* Here c is the equivalent concentration and β is an empirical constant designed to take account not only of the linear effect of ionic size as sketched above, but, in addition, a more important and more general phenomenon known as the **salting out effect,** which involves the solvent as well as the solute.

* It should be noted that Eqs. ($193u''$, v, and w) employ but one arbitrary constant Recently Scharer[1] has shown that the solubility results for $TlCl$, Ag_2SO_4, $CaSO_4$, and two cobaltammine salts, one of the triunivalent type, when dissolved in salts of various types, can be accurately accounted for up to concentrations as high as 0.3μ in the case of $CaSO_4$, by employing values of b in Eq. ($193u''$) of the order of $1–5 \cdot 10^{-8}$ *cm.*, a result which indicates that the arbitrary constant actually has the general theoretical significance of an ionic diameter (*cf.* **191a**).

* In calculating the effect of interionic forces on the irreversible process of conduction, Debye and Huckel point out in their second paper that account must also be taken of the electrostatic drag (cataphoresis effect) which a charged ion exerts upon the solvent molecules surrounding it (*cf.* **244** and **245**). As the ion moves through the medium, the solvent molecules must orient themselves in respect to the ionic field and then become disordered again after the ion has passed. This involves a time factor, the time necessary for the water molecules to relax into their unoriented state. This factor, as well as the one due to a distortion of the field caused by the motion of the ion, operates as a brake upon the ionic mobility. A consideration of both factors yields a complicated expression, again involving κ or $\sqrt{\mu}$ as for the reversible processes mentioned above, which shows that the conductivity coefficients of salts of the same valence type should not be the same even in the range of ideal salt solutions, as is the case with thermodynamic properties, since the effects of the electrical forces depend upon the limiting mobility of the ions. They show that their equation is in excellent agreement with the best conductivity data for aqueous solutions[2] and in fair agreement with the conductivity data for non-aqueous solutions.

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[1] * *Physik Zeit*, **25**, 145 (1924)

[2] * That of Wieland (*J Am Chem Soc*, **40**, 138 (1918)) on KCl and the classical results of Kohlrausch and Maltby yielding the square-root law.

* The evidence obtained thus far agrees so well with the theory that it seems reasonable to accept the Bjerrum assumption that typical strong electrolytes (salts) are practically completely dissociated at all concentrations, at least in solvents of high dielectric constant. If this conclusion is not accepted then it becomes difficult to reconcile results like those given in Fig. 51*c*, because many of the very minor deviations still unaccounted for lie in a direction opposite to that which would be caused by a chemical association into neutral molecules, and what would be expected on purely kinetic grounds on the basis of such an hypothesis.

189. The Apparent Degree of Dissociation of Strong Electrolytes in Different Solvents.—From the preceding discussion the difference between the true and apparent degree of dissociation must increase the greater the electric forces acting between the ions. Now the force between two electrically charged particles e_1 and e_2 separated by a distance r amounts according to Coulomb's law to

$$\mathfrak{K} = \frac{e_1 e_2}{r^2 D}, \tag{194}$$

where D is the dielectric constant of the separating medium. For molecules at equal distances, $\mathfrak{K}$ is therefore greater, and $\alpha - \alpha'$ and $\alpha - \alpha''$ likewise greater, the greater the charge on the ions and the smaller the dielectric constant. Since α is practically equal to unity, α'' should, therefore, be smaller the greater the ionic charge and the smaller the dielectric constant.

Both expectations are well established by experience. The apparent degree of dissociation α'' decreases with increasing valence of the ions, for example, in $\frac{1}{30}$ N solution α'' amounts to 0.91 for KCl, 0.81 for K_2SO_4, 0.76 for $K_3Fe(CN)_6$, 0.69 for $K_4Fe(CN)_6$, and 0.53 for $ZnSO_4$.

Walden determined the apparent degree of dissociation of a suitable salt, namely, tetraethylammonium iodide in a number of solvents of differing dielectric constants. The results are epitomized in Table 38, which shows the expected parallelism between α'' and the dielectric constant D.

TABLE 38.—APPARENT DEGREE OF DISSOCIATION OF TETRAETHYLAMMONIUM IODIDE

Solvent	Dielectric constant	$\alpha'' = \frac{\Lambda_c}{\Lambda_\infty}$	
		$c = 0.01$	$c = 0.001$
Water	81.7	0.91	0.98
Nitrobenzene	35.4	0.71	0.88
Ethyl alcohol	25.2	0.54	0.78
Acetone .	21.4	0.50	0.74
Benzaldehyde	18.0	0.51	0.73
Salicylic aldehyde	13.9	0.34	0.55

190. The Behavior of Strong Acids.—The strong inorganic and organic acids must stand between the neutral salts and the weak organic acids as regards the magnitude of their true degree of dissociation, since all acids are but little dissociated in the pure liquid state, while, on the contrary, salts are highly dissociated. There is no basis for the assumption that this relation would be reversed in solution. But it is noteworthy that the apparent degrees of dissociation α' and α'' are greater with strong acids than with neutral salts (*cf.* Table 39).[1]

TABLE 39.—APPARENT DEGREE OF DISSOCIATION OF HYDROCHLORIC ACID

Concentration	α' (freezing point)	α'' (conductivity)	$\frac{\alpha''^2}{(1-\alpha'')v}$
0.00025		0.9984	0.16
0.0005		0.9970	0.17
0.001		0.9940	0.17
0.002		0.9922	0.26
0.005	0.989	0.985	0.33
0.01	0.972	0.976	0.41
0.02	0.954	0.967	0.57
0.05	0.930	0.948	0.86

From this the conclusion is drawn that the corrections $\alpha - \alpha'$ and $\alpha - \alpha''$ are smaller with strong acids than with neutral salts. At very high dilutions, where these corrections are small for neutral salts, they appear to be diminished to such an extent with acids that the measured values of α' or α'' may be substituted directly in the L M A.

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[1] *See footnote 184.

Thus, the expression $\frac{\alpha''^2}{(1 - \alpha'')v}$ shows a satisfactory constant at concentrations below N/30 with dichloracetic acid and below N/100 with trichlorbutyric acid. A more or less constant value can be recognized for trichloracetic acid and even with hydrochloric acid at high dilutions, even though, owing to the uncertainty involved in Λ_∞, α'' can only be determined approximately. From this behavior it appears that the ions influence one another only a little with the strong acids at very high dilutions, just as with the weak acids at less dilution, i e, the forces between them disappear

An explanation for this would necessitate the assumption of an especially great hydration of hydrogen ion, which, indeed, stands in excellent accord with the considerations of **244** (see BJERRUM, *Z. anorg Chem*, **109,** 275 (1920), in English in *Meddel Nobelinst*, **5,** No. 16 (1919)). Evidently, the envelope of water surrounding the H˙ ion screens off the electrostatic forces exercised by the neighboring ions (similar to a Faraday cage) completely at great dilutions and at least partly at lesser dilutions

TABLE 40 - APPARENT DEGREE OF DISSOCIATION OF SEVERAL STRONG ORGANIC ACIDS

$c = \frac{1}{v}$	Dichloracetic acid		Trichlorbutyric acid		Trichloracetic acid	
	α''	K	α''	K	α''	K
$1/32$	0.708	0.0538	0.850	0.152	0.9014	0.257
$1/64$	0.803	0.0512	0.903	0.132	0.927	0.186
$1/128$	0.878	0.0196	0.941	0.117	0.943	0.122
$1/256$	0.931	0.0194	0.966	0.107	0.963	0.097
$1/512$	0.963	0.0196	0.983	0.111	0.979	0.091

191. Repression of Electrolytic Dissociation by Excess of One Ionic Species. Indicators.—Electrolytic dissociation equilibria, *in so far as they obey the law of mass action*, behave just as do the equilibria of gaseous substances (see **180**), which dissociate into different constituents. Thus the electrolytic dissociation of a weak electrolyte is repressed by an excess of one of the ions arising from the dissociation. This phenomenon is particularly easy to observe with substances whose neutral molecules possess colors different from that of their ions. A relatively small excess of one of the ions suffices for the production of a color change with sufficiently weak acids or bases whose neutral molecules and ions have different colors.

A weak acid whose anion and neutral molecule are differently colored can, therefore, serve for the determination of the H^+ concentration of a solution. Low concentrations of H^+ ion favor the dissociation and permit the color of the anions to develop. A greater H^+ ion content represses the dissociation so far that the color of the anion disappears and only that of the neutral molecules remains. Such substances, which are very important for analytical purposes, are designated as *indicators.*

Paranitrophenol, whose anion is colored a deep-yellow, while the neutral molecule is colorless,[1] is an example of such an acid indicator Therefore, at low H^+ ion concentration (neutral or alkaline reaction) the paranitrophenol appears yellow, and, conversely, at high H^+ ion concentration (acid reaction) colorless Weak bases, whose cation shows a color different from that of the neutral molecule, may be used as indicators in a similar manner; methyl orange is an example of a basic indicator

Since the establishment of the true neutral point depends, as a rule, upon the practical application of indicators, an indicator would appear to be the more useful:

1. The closer the color change coincides with the H^+ or OH^- ion concentrations of pure water (0.78×10^{-7} at 18°) (*cf.* Table 34).
2. The sharper the change in color.

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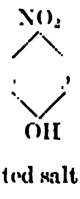
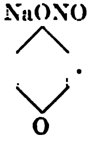
[1] It can be proved in nearly all cases that the color change appearing on dissociation is connected with an internal rearrangement of the molecule; for example, the neutral (colorless) paranitrophenol possesses the formula



while the (colored) highly dissociated salt possesses a quinoidal constitution:



In order to comply with the first requirement, the indicator must not be too strong an acid or base, else a relatively large excess of H^+ or OH^- ions would be necessary to produce a color change. On the other hand, the strength of the indicator as an acid or base may not be too small, else the appearance of hydrolysis will be noticeable (**193**), which likewise exerts a displacement of the point of color change.

The following table gives a synopsis of the behavior of the more common indicators:

TABLE 41[1]

Common name	Chemical name	Color change	$-\log [H^+] = P_H^+$
Thymol blue			
Acid range	Thymol sulfon pthalein	Red-yellow	1.2–2.8
Alkaline range	Thymol sulfon pthalein	Yellow-blue	8.0–9.6
Bromphenol blue	Tetrabromphenol sulfon pthalein	Yellow-blue	3.0–4.6
Methyl orange	P-benzenesulfonic acid azodimethyl aniline	Orange-red-yellow	3.1–4.4
Methyl red	O-carboxybenzene azodimethyl-aniline	Red-yellow	4.4–6.0
Bromcresol purple	Dibromo-o-cresol sulfon pthalein	Yellow-purple	5.2–6.8
Bromthymol blue	Dibromothymol sulfon pthalein	Yellow-blue	6.0–7.6
Litmus.		Red-blue	4.5–8.3
Phenol red	Phenol sulfon pthalein	Yellow-red	6.8–8.4
Cresol red	O-cresol sulfon pthalein	Yellow-red	7.2–8.8
Phenolpthalein	Phenolpthalein	Colorless-red	8.3–10.0
Thymolpthalein	Thymolpthalein	Colorless-red	9.3–10.5

[1] * Revised by the translators largely from CLARK, "Determination of Hydrogen Ions"

It is to be observed that in the titration of the weaker acids and bases the indicators indicate only the H^+ or OH^- ion concentration and the concentration of the undissociated acidic or basic molecules. If the H^+ or OH^- ions were completely liberated from the dissociated molecules during the titration, no great disturbance would be produced. But this is not the case with weak acids and bases, where, due to the effect of the ions of the water, an appreciable complication ensues (see **193**).

The dissociation of pure water is also repressed by an excess of one of its dissociation products, be it H^+ or OH^- ions, and the following relation exists:

$$\frac{[H^+]\,[OH^-]}{[H_2O]} = Const. \quad \text{or simply} \quad [H^+]\,[OH^-] = K_{H_2O}. \quad (195)$$

since the concentration of water in dilute solutions is practically constant.

Whereas $[H^+]_n = [OH^-]_n$ in a neutral solution, $K_{H_2O} = [H^+]_n^2 = [OH^-]_n^2$, the OH^- ion or H^+ concentration in an alkaline or acid solution are unequal. Now the measurement of very small concentrations is possible according to the method of concentration cells (see **217**) by the use of two hydrogen electrodes, one of which dips in an acid solution whose concentration $[H^+]_s$ is known approximately, while the other dips in an alkaline solution of known OH^- ion content $[OH^-]_a$, but of unknown H^+ ion content $[H^+]_a$, *i.e.*, a so-called acid-alkali cell.

$$E = 0.1983 \cdot 10^{-4} T \, log \frac{[H^+]_s}{[H^+]_a} = 0.1983 \cdot 10^{-4} T \, log \frac{[H^+]_s [OH^-]_a}{K_{H_2O}}. \qquad (196)$$

Since in Eq. (196), E, $[H^+]_s$, and $[OH^-]_a$ may be directly determined, the L.M.A. for the electrolytic dissociation of water, contained in Eq. (196), may be experimentally verified by these measurements.

*When the attempt is made to apply the treatment given above to strong electrolytes, whose true degree of dissociation is generally unknown, it is found that the L.M.A. in its classical form breaks down completely. Thus when an excess of NaCl is added to a 0.01 HCl solution,[1] the potential of the H^+ ion as measured by the hydrogen electrode is greater than it was before the addition of NaCl, which is exactly opposite to what would be expected from the addition of a common ion.

*Figures 51*d* and *e*, taken from the extensive investigations of Harned,[2] show some of the marked effects which neutral salt additions have on the activity coefficient of HCl. In Fig. 51*d* the concentration of HCl is held constant at 0.10M. In Fig. 51*e* both the HCl and KCl concentrations are varied.

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[1] * This can be demonstrated very easily by adding to the solution a few drops of the indicator thymol blue. The addition of NaCl then produces a red color indicating a higher acidity. In using indicators for such purposes, however, it should always be kept in mind that they are also electrolytes, and are consequently subject to salt errors just like other electrolytes. Recent work has shown that the effect of salts on the color of indicators is to be interpreted as shift in the equilibrium between the colored and colorless forms, owing to the influence of the electrical effects described in **188b**, **c**, **191a**. (*Cf.* BRONSTED, *J. Chem. Soc.*, **119**, 574 (1921))

[2] * HARNED and BRUMBAUGH, *J. Am. Chem. Soc.*, **44**, 2729 (1922) and earlier papers; see also the chapter on "Electrochemistry of Solutions" by Harned in TAYLOR's "Treatise on Physical Chemistry," D. Van Nostrand Co. (1924).

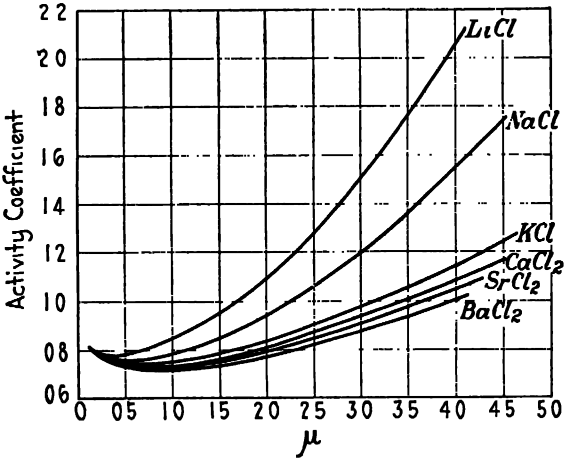

FIG. 51*d*

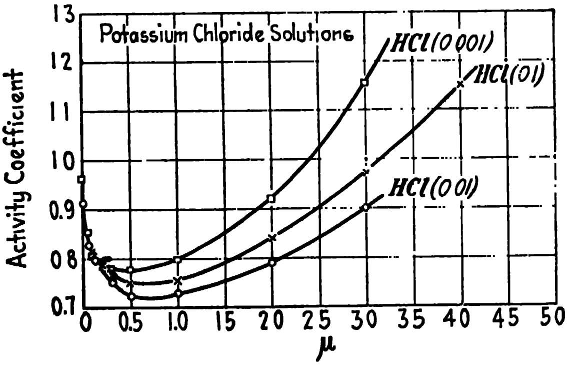

FIG 51*e*

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*There may perhaps be some slight repression of the ionization of certain strong electrolytes like HCl, but this factor, if it exists at all, is completely overshadowed by the electrical effects between the ions and the solvent. Thus in a 4.0M LiCl solution, 0.1M HCl would appear on the classical theory to be 200 per cent ionized, an obvious impossibility! It is best, therefore, to speak only in terms of the activities or escaping tendencies of ions and not their concentrations when dealing with solutions containing appreciable quantities of ions. When this is done the L.M.A. and all its corollaries are universally valid.

*In order to explain the increase in the activity coefficients of ions at high concentration, it will be advantageous to discuss first the simpler case of the activity coefficient of neutral substances when dissolved in strong salt solutions.

***191a. The Salting Out Effect.**—It is well known that the addition of neutral salts to an aqueous solution containing an electrically neutral substance like ether, H_2, or N_2O gas usually results in a decrease in the solubility of the neutral substance.

*The specific solubility effects, which concentrated solutions of $NaCl$, $(NH_4)_2SO_4$, and Na_2SO_4 exert, are made use of in the separation of proteins and in the commercial manufacture of dyestuffs and soaps. Although, in general, this phenomenon is a complicated one depending upon the specific properties of the neutral molecule and of the added salts, it has been found empirically that a linear relation between the logarithm of the solubility ratio and the concentration of added salt often holds for a considerable range (up to about 4.0M) of salt additions; namely

$$log \frac{s}{s_0} = k_s c, \tag{193x}$$

where k_s, the salting out coefficient, is a constant for each particular salt when salting out a given neutral substance. s is the solubility in the salt solution of concentration c and s_0 is the solubility in pure water.

*Now Eq. (193j) permits the substitution of $-$ *log* f for *log* $\frac{s}{s_0}$ and Eq. (193x) then becomes

$$-log\, f = k_s c. \tag{193x'}$$

*From a consideration of Eq. (193d), it may be said that *the change in the chemical potential of a neutral molecule is usually a linear function of the concentration of the salt which has been added to the solution.*

*Succinic acid exists almost entirely as the undissociated molecule in a saturated aqueous solution and Fig. 51*f*[1] illustrates the effects of the addition of neutral salts upon its solubility. The relation between *log f* and the molar concentration is almost linear, as demanded by Eq. (193*x*). With succinic acid, 4.0M LiCl reduces the solubility from 0.197M in pure water to 0.135M, or 72 per cent, while 2.4M KI actually increases the solubility some 10 per cent.

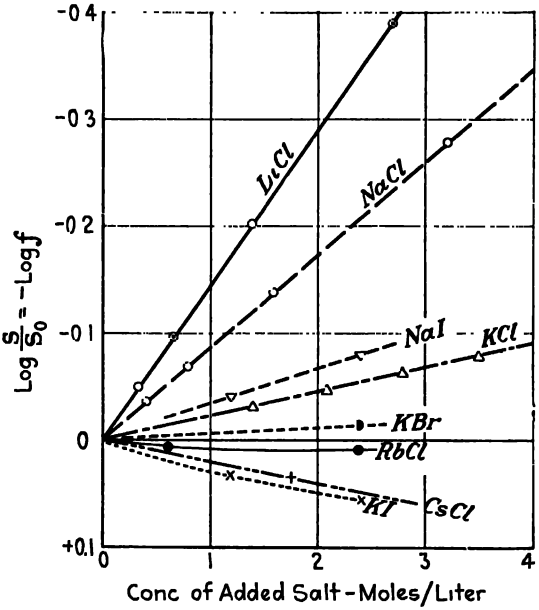

FIG 51*f*

*When the anion of the added salt is the same but the cation is varied, it is found that the values of k_s usually form the following series:

Li Na K Rb Cs

$\longleftarrow$

Increasing negative values of k_s.

---

[1] * Taken from the work of K. Linderstrom-Lang, *Compt.-rend. trav. lab. Carlsberg*, **15**, No. 4, 1 (1924) (in English). This paper contains not only a comprehensive review of the work of previous writers but also contains many new experimental data. Certain aspects of the theory given below are developed in this paper.

*In Eq. (193x) negative values of k_s represent a positive salting-out effect; positive values, a dissolving power greater than that of pure water. The general order of the anions of the potassium salts is

$$\underleftarrow{\mathrm{SO_4 \quad Cl \quad Br \quad I \quad SCN}}$$

Increasing negative values of k_s,

i.e., sulfates and Li salts show in general the greatest precipitating power, while thiocynates and Cs salts show the least, or in some cases a dissolving power greater than that of water. The absolute value of k_s depends upon the nature of the neutral substance as well as upon the salts. These relationships, which are quite general, at once recall the familiar Hofmeister series of colloid chemistry, with which phenomena they are closely connected.

*When the activity coefficients of pure solutions of LiCl, NaCl, KCl, and CsCl are plotted against the concentration, or, better, $-\log f$ against the square root of the ionic strength as given in Fig. 51g,[1] it is found that the values of $-\log f$ follow almost exactly the same general course at high concentrations as do the values for $-\log f_{(HCl)}$ for dilute solutions of HCl (0.10M) to which the various alkali chlorides have been added.

*The increase in the value of f (or more negative values of $-\log f$) which occurs in highly concentrated solution is almost invariably of the same general order as are the values of k_s for the same ions when acting upon neutral molecules. From this and other considerations it follows that ions exercise a salting-out effect upon other surrounding ions just as they do upon neutral molecules. The chief difference is that the salting-out effect of ions upon ions, which becomes noticeable at higher concentrations, is superimposed upon the primary electrical attractions exerted between ions, as described in **188b, c,** while in the salting-out effect of ions upon neutral molecules no primary electric attractions corresponding to Eq. (193u'') exist; the salting out effect in this case appears simply as a linear function of concentration uncomplicated by other phenomena.

*It is accordingly necessary to add a salting-out term ($k_s c$) to Eq. (193u'') if it is desired to account for the activity coefficients of concentrated electrolytes. For a general equation of the behavior of strong electrolytes, then,

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[1] *In Figs. 51d, e, $f_{(HCl)}$ for these mixtures is plotted against μ instead of $-\log f_{(HCl)}$, but the general shape of the curves remains the same.

$$-\log_{10} f = \frac{3}{2.3}\alpha z_1 z_2 \sqrt{\mu}\left(\frac{1}{1 + \kappa b}\right) + k_s c. \qquad (193y)$$

Recent calculations by Huckel show that the activity coefficients of HCl, LiCl, NaCl, and KCl solutions as determined by *e.m.f.* and freezing-point measurements may be satisfactorily represented from infinite dilution up to the concentrations of the saturated salt solution by such an equation.

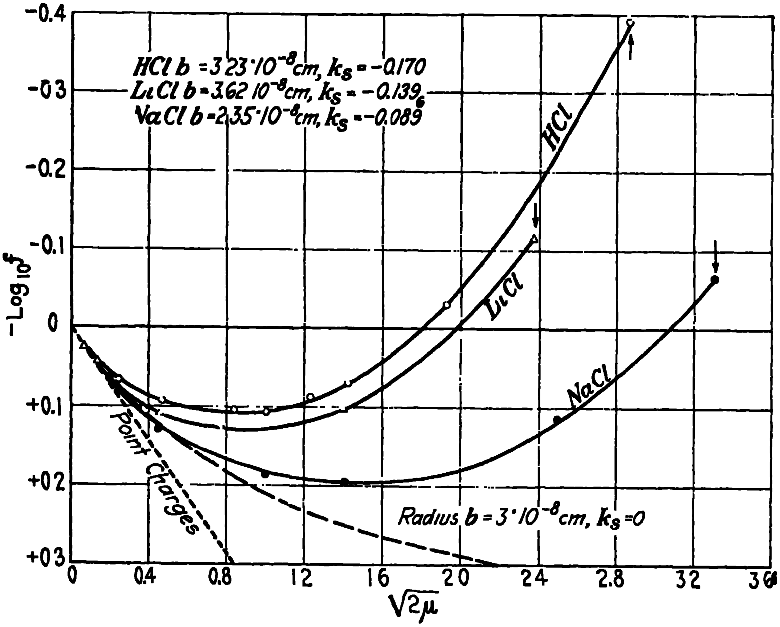

Fig 51g [1]

*The straight, broken line in Fig. 51*g* corresponds to Eq. (193*u*), or to line *I* in Fig. 51*c*; it is consequently the equation for a uniunivalent electrolyte when its ions are considered as point charges. The curved dotted line represents the values of the activity coefficient when the ions have an average value of $b = 3 \cdot 10^{-8}$ *cm*. The curvature of this line is due to the factor $\frac{1}{1 + \kappa b}$

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[1] * In Fig 51*g* the *b* refers to the average effective diameter and not the radius

in Eqs. (193u) and (193y), the salting-out effect being considered as zero. The departure from the point charge equation is, therefore, greater as b becomes greater. It is apparent that the influence upon the primary electric effect even when the ionic size is as large as $b = 3 \cdot 10^{-8}$ *cm.* cannot begin to account for the experimental data when the concentration exceeds 0.5M. The inadequacy of the factor of ionic size on the primary electric effect becomes more apparent when it is noted at higher concentrations that the ions which have the smallest radii, as determined by X-ray analysis and the Bohr theory (Sec. D), depart the most from the point charge equation. A theoretical consideration of the causes of the salting-out effect shows that the value of k_s is inversely proportional to the ionic radius, so that the last term in Eq. (193y) becomes larger the smaller the radius.

*The heavy lines in Fig. 51g represent the theoretical result for the general Eq. (193y) when the values given in the legend for b and k_s are introduced. Huckel[1] calculates the value of b from the experimental data[2] in dilute solutions by the use of an equation like Eq. (193u'') and the values for the salting out coefficient k_s from the data for the highest concentration. Since the values of b agree with what would be expected for the effective ionic diameter of such ions in solution, and since the experimental data at intermediate concentrations agree with those given by the equation, Eq. (193y) may be considered as established for uniunivalent electrolytes.

*Huckel explains the salting-out effect of ions upon ions qualitatively as follows: from an atomistic standpoint it is clear that the electrical properties of ions cannot be expressed entirely by the simple assumption made in **188c**, namely, that ions are *rigid spheres* upon which the electricity is uniformly distributed; instead, the actual structure of the ion must be considered for a complete picture of the theory of salt solutions. From the Bohr theory (*cf.* Sec. D) it is evident that the orbits which electrons describe in the atom may be deformed to a greater or less extent when the ion is exposed to the intense electrical fields set up by surrounding ions. These fields are of the order of 10^6 *volts* at $3 \cdot 10^{-8}$-*cm*. distance. In a medium of high dielectric constant like water ($D = 81$) this phenomenon, which appears in addition to the ordinary Coulomb forces between ions, will result, as a rule, in a repulsive instead of an attractive force being set up between the ions. (*Cf.* **351.**)

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[1] * *Physik. Zeit.*, **26,** 93-147 (1925).

[2] * The experimental data represented by the points were obtained through the use of e m f measurements on cells without transport: for HCl by Ellis, *J. Am Chem Soc.*, **38,** 737 (1916); Noyes and Ellis, *ibid.*, **39,** 2532 (1917); and Linhart, *ibid.*, **41,** 1175 (1919); for NaCl by Allmand and Pollack, *J. Chem Soc.*, **115,** 1020 (1919); for LiCl by MacInnes and Beattie, *J. Am. Chem. Soc.*, **42,** 1117 (1920).

* For example, a charged metallic sphere suspended in air or in vacuum where $D = 1$ always attracts surrounding neutral bodies, say another uncharged sphere or a bit of paper, owing to the opposite charges which are induced upon the latter. That is, the neutral bodies are subjected to forces which tend to drive them to a point where the absolute value of the electrical field is the greatest. However, the electrical charges which have been induced upon the neutral body are not rigidly bound to the electric center of the body but are displaced under the influence of the electric forces. The neutral body is "*polarized,*" and this polarization always results in an attractive force.

* On the other hand, if the same experiment is carried out, not in air, but in a medium like water, whose dielectric constant is greater than that of the neutral body, it will be found that a repulsive force will be exerted between the charged sphere and the neutral body. Owing to the electric field set up by the charged sphere, both the water and the neutral body will be polarized but since the former has the greater dielectric constant it is more easily polarized and therefore attracted the most. Water molecules will consequently congregate in the neighborhood of the charged sphere at the expense of those neutral bodies having dielectric constants lower than $D = 81$. The charged sphere and neutral body will accordingly be squeezed apart and it will appear as though a repulsive force were being exerted between them.

* A quite similar state of affairs holds for an aqueous solution of ions after we have taken account of the primary effects described in **188c.**

* The dielectric constant of the ions depends upon the ease with which the outer electron orbits can be deformed by an electric

field. The optical data of Heydweiller[1] show that the electron orbits of the Cs^+ ion are more easily deformed than are the orbits of the smaller ions like Li^+ and Na^+. Li^+ ion, consequently, has the lower polarizability. The dielectric constant of water is due not only to the polarizability of its O and H atoms, a phenomenon which is independent of temperature, but also to the distribution of the charges in the H_2O molecule. Since this distribution is not symmetrical, as is the case with simple ions like Na^+, K^+, Cl^-, etc., which possess the structure of the rare gases, a water molecule must therefore be considered as an electrical dipole.[2]

*The electric moment of the water dipole is the primary cause of the exceedingly high dielectric constant of water, since the dipoles must set themselves in an electrical field just as the elementary magnetons in a magnetic body do in a magnetic field. It may be added that since the thermal agitation of the molecules tends constantly to upset the orientation of the dipoles in the field the dielectric constant of water will decrease with rising temperature as accords with the experimental data.

*From these considerations it is clear that a Li^+ ion should be "salted out" by surrounding Li^+ ions much more than would be true of Cs^+ ions in the presence of Cs^+ ions. The same argument holds true for Cl^- ions as opposed to I^- ions, since the electronic structures of these ions corresponds to those for K^+ and Cs^+ ions. The marked difference in the value of k_s for CNS^- ions as compared to Cl^- ions would appear to be due to the difference in symmetry of the two ions. The CNS^- ion for this reason should possess a greater dielectric constant and therefore induce greater dissolving properties. The salting-out properties of the $SO_4^{=}$ ion are most likely due to its divalent character.

*On the basis of the considerations sketched above, Debye and Huckel have derived a theoretical equation for the evaluation of the salting-out term which involves primarily the change in dielectric constant and the reciprocal of the ionic size.[1] Although their equation is composed of several complex concentration terms, the sum proves to be an almost linear function of the concentration as demanded by the empirical equations (193x, 193y). However, the data available at present are too scanty to afford a thorough test of the validity of the theoretical equation, and it will not be discussed any further at this time.

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[1] * *Ann. Physik*, **41, 48,** and **49** (1913-16); also FAJANS and JOOS, *Z. Physik.*, **23,** 6 (1924).

[2] * *Cf* L EBERT, *Z physik. Chem.*, **113,** 1 (1924) for a discussion of the different varieties of polarization in complex molecules. Also DEBYE, MARX, "Handbuch der Radiologie," VI, pp 597 *et seq*, Leipzig (1925)

192. Dissociation in Steps.—If the molecule of a weak electrolyte is able to split off several ions, the dissociation usually proceeds in steps, *i.e.*, first one ion dissociates at low dilution, as in a binary electrolyte, and the second comes off at a higher dilution. Dibasic malonic acid, which dissociates practically only one H^+ up to a dilution of N/100, serves as an example, so that the affinity constant may be calculated up to this point as for a monobasic acid. The second H^+ ion is split off at higher dilutions, which becomes noticeable through deviations from the simple formula (Eq. (193)).

The two H^+ ions are also bound unequally in carbonic acid (H_2CO_3); the dissociation at first is $H_2CO_3 \rightleftarrows H^+ + HCO_3^-$, while at considerably higher dilution the reaction $HCO_3^- \rightleftarrows H^+ + CO_3^{=}$ is substituted.[2]

Stepwise dissociation is especially striking in a group of salts which are classified under the term **complex salts,** and for which potassium silver cyanide ($KAg(CN)_2$) represents the best-known example. Over a considerable range in aqueous solution the molecule dissociates[3] first according to the scheme

$$KAg(CN)_2 \rightleftarrows K^+ + Ag(CN)_2^-,$$

but the dissociation

$$Ag(CN)_2^- \rightleftarrows Ag^+ + 2(CN)^-$$

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[1] * The minute change in volume caused by salt additions also plays a minor rôle in the theoretical equation

[2] In many cases it is not necessary for the explanation of these phenomena to assume that the second H^+ ion is more firmly bound through chemical forces or the like than the first, for the electrostatic attraction between them is already greater for the second step yielding divalent ions than for that of the first step. * See BJERRUM, *Z. physik. Chem.*, **106**, 219 (1923).

[3] * As a strong electrolyte.

takes place only to a minute degree, so that the silver-ion content of a $KAg(CN)_2$ solution is extraordinarily small. The constant of mass action is

$$\frac{[Ag^+]\,[CN^-]^2}{[Ag(CN)_2^-]} = \text{approx. } 10^{-21}. \tag{197}$$

If $[Ag(CN)_2^-] = 1$, we get, without excess of CN^- ion: $[Ag^+] = [CN^-] = 10^{-7}$, but, on the contrary, if $[CN^-] = 1$, then $[Ag^+] = 10^{-21}$!

In other cases the difference between the different steps is less striking. Sometimes the splitting off of both (metallic) ions results almost simultaneously. It is obvious in this case that we are concerned either not at all or only to a slight degree with the formation of complex ions, and, instead, this substance represents only a mixture of two ordinary salts in a definite ratio, crystallizing together. Alum is an example of such a **double salt** whose empirical formula is, indeed, completely analogous to that of potassium silver cyanide, though here, in contrast to potassium silver cyanide, both of the metallic ions always appear in about equal concentration.

193. Hydrolysis.—The ionic equilibria which appear in aqueous solution enter into the dissociation equilibrium of water, similar to those cases mentioned in **181.** This is known as **hydrolysis** and is an important phenomenon in numerous inorganic reactions

A solution of a completely dissociated neutral salt, such as sodium acetate, may be considered, whose cation represents the radical of a strong base, and whose anion, on the contrary, represents that of a weak acid. The dissociation equilibrium

$$NaAc \rightleftarrows Na^+ + Ac^-$$

occurs in solution; the H^+ ion dissociated from the water unites partly with the Ac^- ion, *i.e.*, the reaction

$$HAc \rightleftarrows H^+ + Ac^- \tag{198}$$

proceeds from right to left until the equilibrium

$$\frac{[H^+][Ac^-]}{[HAc]} = K_{HAc} \tag{198a}$$

is attained.

Inasmuch as this reaction consumes H^+ ion, a corresponding amount of OH^- ion must be freed, according to Eq. (192), so that the solution becomes alkaline, and in fact, forms almost the same quantity of OH^- ions as undissociated HAc molecules. Therefore, the hydrolytic reaction may be represented by the reaction equation

$$Ac^- + H_2O \rightleftharpoons HAc + OH^-. \qquad (199)$$

The calculation of the OH^- concentration takes the following form:

Since $[H^+]$ must have the same value in Eqs. (195) and (198*a*), a division of both equations is permissible, resulting in

$$\frac{[HAc][OH^-]}{[Ac^-]} = \frac{K_{H_2O}}{K_{HAc}} = K_{hydrolysis}$$

a relation which simultaneously represents the equilibrium condition for reaction Eq. (199), since $[H_2O]$ is to be considered as constant. It is observed that $[OH^-]$ and $[HAc]$ are equal, from which

$$[OH^-] = \sqrt{\frac{K_{H_2O}[Ac^-]}{K_{HAc}}}. \qquad (200)$$

For a solution normal in respect to Ac^- ions, from Table 34 and **187** the values indicated for HAc at 18° are obtained:

$$[OH^-] = \sqrt{\frac{0.60 \cdot 10^{-14}}{18 \cdot 10^{-6}}} = \sqrt{3.3 \cdot 10^{-10}} = 1.8 \times 10^{-5} \textit{ mole/l.}$$

i.e., 1.8×10^{-5} *mole/l.* of Ac^- ion react according to Eq. (199), or the sodium acetate is hydrolyzed to the extent of 0.0018 per cent. At higher temperatures the degree of hydrolysis markedly increases, owing to the increase in K_{H_2O}; for example, at 100°C. it amounts to about ten times its value at 18°C. The OH^- ion concentration is already so considerable that some metallic salts are precipitated from solution as hydroxides.

As the acid whose anion corresponds to that of the salt becomes weaker, the hydrolysis becomes greater. Boric acid ($K = 6.6 \cdot 10^{-10}$), hydrocyanic acid ($K = 13 \cdot 10^{-10}$), and phenol ($K = 1.3 \cdot 10^{-10}$) serve as examples of some especially weak acids. The degree of hydrolysis amounts, correspondingly, in $\frac{N}{10}$ solution to 1.5 per cent for sodium borate, 1.12 per cent for potassium cyanide, and 3.05 per cent for potassium phenolate. Carbonic acid is even weaker than the acids mentioned—at least, in respect to the dissociation of the second H^+ ion. The degree of hydrolysis of sodium carbonate amounts to 3.17 per cent, so that an aqueous solution of this salt reacts quite strongly alkaline.

K_{hyd}, and hence K_{H_2O}, can be calculated, if K_{HAc} is known, according to various methods, by measuring the OH^- ions by means of indicators or by the *e m.f.* of concentration cells. The values for the H^+ ion concentration in neutral solution given in Table 34, column 5, have been determined by this procedure. Obviously, it is exactly analogous to the procedure described in **181.**

Hydrolysis also occurs if we prepare an aqueous solution of a salt, produced by the union of a weak base and a strong acid, except that OH^- ion enters in place of H^+ ion in the preceding discussion. Such aqueous solutions, therefore, contain free H^+ ions and react more or less acid; thus, NH_4Cl exhibits an acid reaction, the degree of hydrolysis being about the same as for sodium acetate When NH_4Cl is added to a weaker base like NH_4OH, many indicators, such as phenolphthalein, therefore, show a color change, as though an acid had been added (see footnote, **185**).

This phenomena creates considerable trouble in the use of phenolphthalein in the titration of NH_4OH with HCl. The NH_4Cl formed renders the solution more acid through its hydrolysis, and, therefore, produces a gradual fading out of the color. The color has already completely disappeared before an equivalent quantity of acid is added. The choice of another indicator (methyl orange), whose change of color takes place at H^+ ion concentrations which lie outside the range of the hydrolysis of NH_4Cl, remedies the difficulty.[1]

When a weak base and a weak acid are involved in the formation of a salt, as is the case with ferric acetate, H^+ as well as OH^-

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[1] * In the titration of a weak acid, such as acetic acid, by means of the stronger bases it is necessary to use an indicator which changes in the alkaline range, such as tropaeolin or phenolphthalein. See HILDEBRAND, J. H. (*J. Am. Chem. Soc*, **35**, 847 (1913)) or the monographs on the "Determination of Hydrogen Ions," by MANSFIELD CLARK (*loc. cit*), or L. MICHAELIS, translated by PERLZWEIG (Williams and Wilkins) for the various types of titration curves and the indicators to be used in each case.

ion are withdrawn from the water to form undissociated acid and base.

$$HAc \rightleftharpoons H^+ + Ac^-; \quad K_{HAc} = \frac{[H^+][Ac^-]}{[HAc]} \qquad (198)$$

$$\tfrac{1}{3}Fe(OH)_3 \rightleftharpoons \tfrac{1}{3}Fe^{+++} + OH^-; \quad K_B = \frac{[Fe^{+++}]^{\frac{1}{3}}[OH^-]}{[Fe(OH)_3]^{\frac{1}{3}}}. \qquad (198b)$$

Combination with Eq. (192) yields the hydrolysis equation

$$\tfrac{1}{3}Fe^{+++} + Ac^- + H_2O \rightleftharpoons \tfrac{1}{3}Fe(OH)_3 + HAc$$

$$K_{hyd} = \frac{[Fe(OH)_3]^{\frac{1}{3}}[HAc]}{[Fe^{+++}]^{\frac{1}{3}}[Ac^-]}. \qquad (201)$$

The four equilibrium constants appearing here, K_{H_2O}, K_{hyd}, K_{HAc}, and K_B, are related to one another by the following:

$$K_{hyd} = \frac{K_{H_2O}}{K_{HAc}K_B} \qquad (201a)$$

The degree of hydrolysis, *i. e.*, K_{hyd}, therefore, becomes greater as K_{H_2O} increases and as K_{HAc} and K_B become smaller Since K_{HAc}, and K_B change but little with temperature, while K_{H_2O}, on the contrary, increases, the degree of hydrolysis is always greater at higher temperature than at lower. This becomes so large at 100° in the particular case of ferric acetate that the solubility of $Fe(OH)_3$ is exceeded and it precipitates.

Since carbonic acid is distinctly weaker than acetic acid, ferric carbonate as well as the carbonates of other trivalent metals are so highly hydrolyzed even at room temperature that it decomposes spontaneously into the hydroxide and carbonic acid. Hydrolysis, accordingly, is the reason for the instability of such compounds in aqueous solution

b. Heterogeneous Equilibrium

194. General.—Heterogeneous equilibria are always treated from the following points of view:

1. The laws of homogeneous equilibria are obeyed within a given phase, and thus the L.M.A. holds for gases and dilute solutions.

2. The generalized distribution law holds for the concentration of the individual substances in the different phases. Thus, the concentration c' in one phase is always a definite function of the concentration c of the same substance in a second phase as

well as of pressure and of temperature, *i.e.*, $c' = f(p, T, c)$ (**159**). For example, in the simple case of two dilute solutions in different solvents the general distribution law reduces to the special distribution law of Nernst, for which $c' = Const. \times c$ a given temperature.

Since the distribution ratio of a substance is completely independent of the quantity present in the individual phases, it follows directly that *heterogeneous chemical equilibrium in contrast to homogenous equilibrium is not influenced by the quantities of reacting substances in so far as these appear in different phases.* A combination of the cases under (1) and (2) always leads, theoretically, to the solution of the problem. The details of this procedure may be explained by a few special cases of heterogeneous equilibria.

195. Equilibrium between One Gas and Several Solid Phases. It is well known that calcium carbonate decomposes into calcium oxide and carbon dioxide, *i.e.*, the reaction

$$CaCO_3 \rightleftharpoons CaO + CO_2 \qquad (202a)$$

proceeds from left to right. Now, it may be assumed that calcium carbonate vaporizes to a slight degree in the undissociated form and that the equilibrium corresponding to that of Eq (202*a*) is set up in the homogeneous gas phase. Also the CaO produced in the gas possesses a very small vapor pressure, so that for the greater part it is precipitated as solid CaO. Indeed, it is probable that the reaction does not actually proceed in this roundabout manner, but, instead, the solid carbonate dissociates directly into the solid oxide and gaseous carbon dioxide; but the equilibrium, as has been emphasized many times previously, must be independent of the path by which it proceeds, so that the assumption that the dissociation proceeds only in the gaseous phase introduces no error.

Now the distribution law connects the two solid phases $CaCO_3$ and CaO and the concentration of these substances in the vapor state. In this case it means that the partial pressures (vapor pressures) or the concentrations in the vapor state are constant at a given temperature. Thus the values [CaO] and $[CaCO_3]$ may be combined in Eq. (202*a*) with the constant K_c', obtaining:

$$[CO_2] = K_c \quad \text{or} \quad p_{CO_2} = K_p. \qquad (202b)$$

Accordingly, at a given temperature *calcium carbonate produces a perfectly definite partial pressure of* CO_2 which is analogous to the ordinary vapor pressure of a substance. Some of the more recent values for the dissociation pressures of $CaCO_3$ at different temperatures are given in the following table:

TABLE 42.—DISSOCIATION PRESSURE OF CALCIUM CARBONATE

T	p, *mm*	Observer
787	0.29	v. KOHNER, Diss., Berlin (1914).
865	2.63	
1006	52	
1073	192	RIESENFELD, *J. chim. physik.*, **7**, 561 (1909).
1123	374	
1181	760	

While the dissociation of carbon dioxide represents a univariant equilibrium according to the phase rule, the following reaction serves as an example of a divariant equilibrium. In contrast to the dissociation of $CaCO_3$, two substances appear in the reduction of iron oxide by hydrogen which exist only in the gas phase, and not as solid bodies

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2. \tag{203}$$

The equilibrium equation for the gas phase reads as follows:

$$\frac{[Fe_3O_4][H_2]^4}{[Fe]^3[H_2O]^4} = K_c'. \tag{203a}$$

However, $[Fe_3O_4]$ and $[Fe]$ possess constant values for a given temperature, so that the equation may be written in the simplified form:

$$\frac{[H_2]}{[H_2O]} = \frac{p_{H_2}}{p_{H_2O}} = K_c = K_p \tag{203b}$$

Equation (203*b*) was verified experimentally by Preuner[1] For example, at $T = 1173°$ he found the following values for the ratio of the equilibria pressures $\frac{p_{H_2}}{p_{H_2O}}$.

$$\frac{13.5}{8.8} = 1.54;\ \frac{18.0}{12.7} = 1.41;\ \frac{37.4}{25.1} = 1.49;\ \frac{54.1}{35.1} = 1.54;\ \frac{71.8}{49.3} = 1.47.$$

The burning of solid carbon to carbon dioxide represents one of the most important technical reactions. The concentration of the carbon disappears from the original expression for the law of mass action $\frac{[C][O_2]}{[CO_2]} = K_c'$, and we have

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[1] *Z. physik. Chem.*, **47**, 385 (1904).

$$\frac{[O_2]}{[CO_2]} = K_c = K_p = K.$$

The quantity of oxygen existing in equilibrium with solid carbon is so minute at temperatures under 2000° that its estimation cannot be accomplished by direct measurement of the oxygen concentration. On the other hand, K can be estimated by the combination of two other equilibria (similar to the cases quoted in **181**) which permit of an experimental determination at 1300°. The first reaction to be considered is the so-called gas-furnace reaction:

$$C_{(\text{solid})} + CO_2 \rightleftarrows 2CO,$$

whose equilibrium was first studied exhaustively by Boudouard. In the presence of solid carbon and at $T = 1300°$ the equilibrium favors the side of carbon monoxide, and at 1 *atm* total pressure only 0.75 per cent CO_2 exists, together with 99.25 per cent CO. For a total pressure of 1 *atm* we have for the equilibrium constant

$$K_{pB} = \frac{p^2_{CO}}{p_{CO_2}} = \frac{(0.9925)^2}{0.0075} = 131$$

The second reaction to be used in the calculation of K is the formation of carbon monoxide from carbon monoxide and oxygen and whose equilibrium constant $K_{pC} = \frac{p^2_{CO}p_{O_2}}{p_{CO_2}}$ was estimated to be 3.66×10^{-14} at 1300° by Nernst and v. Wartenberg. By division

$$K = \frac{K_{pC}}{K_{pB}} = \frac{p_{O_2}}{p_{CO_2}} = \frac{[O_2]}{[CO_2]} = 2.79\ 10^{-16} = 10^{-15.54}. \tag{204}$$

The examples quoted for univariant and divariant equilibria yield the same result; namely, that *the concentration of those substances which exist as solid bodies are always eliminated from the equation of mass action applicable to the gas phase.* This may be extended directly to all other heterogeneous equilibria.

196. Equilibrium between a Solution and Several Solid Phases.—Anthracene (c_1) and picric acid (c_2) unite partially in alcoholic solution to form a loose compound, anthracene picrate (c), for which the following equilibrium holds:

$$\frac{c_1c_2}{c} = K_c. \tag{205}$$

In case the rather difficultly soluble picrate is present in solid form, the equation reduces to $c_1c_2 = Const.$ In case anthracene appears as a solid, we have

$$\frac{c_2}{c} = K_c'. \tag{205a}$$

Should picrate as well as anthracene exist together in the solid phase, then only $c_2 = K_c''$ remains, *i.e.*, picric acid can remain in solution only at a given concentration. Should little exist originally, then the reaction

$$\text{Solid picrate} \rightleftarrows \text{picric acid} + \text{solid anthracene}$$

proceeds from left to right or in the opposite direction if more picric acid exists in the solution at first than corresponds to the condition $c_2 = K_c''$. If Eq. (205) is applied to substances which dissociate into ions in solution, then the following will hold in the presence of a solid body whose concentration c is constant:

$$c_1c_2 = Const = K_{sp}, \tag{206}$$

where c_1 and c_2 represent the concentration of the ions. The constant in this special case is usually designated as the **solubility product** of the ions.

It appeared doubtful from the very first whether Eq. (206) would be applicable for strong electrolytes for which the law of mass action in its usual form fails to work. As was shown in **188**, the failure of the law of mass action for strong electrolytes may be due in part to the fact that the concentration c of the undissociated portion is not correctly estimated by the usual methods. However, in the present case, where c remains constant, this uncertainty disappears completely, so that the law of mass action in the *simplest form* which is assumed for the dissociation of salt in the presence of one solid substance may lay claim to at least *approximate* validity for strong electrolytes.

In fact, Eq. (206) may be established by experiments on very difficultly soluble salts. Since very small ionic concentrations are frequently involved, the concentration-cell method mentioned in **183e**, and described in greater detail in **212**, is used for the measurement. If the solubility is not too small, satisfactory results can be obtained by the conductivity method (**183d**). For example, for $AgIO_3$, W. A. Roth found, according to the latter method, that the product c_1c_2 gave values between 1.45 and 1.60×10^{-8} for an approximately sevenfold excess of IO_3^- ion over that of the Ag^+ ion.

The values of the solubility products K_{sp}, which are so important for the application of Eq. (206), may be obtained simply from the saturation concentration c_0 of the difficultly soluble salt in the pure solvent without a knowledge of the individual ion concentrations. It may be assumed that the total concentration c_0 of the salt is the same as the total concentrations of the individual ions c_1 and c_2, since the undissociated portion of almost completely dissociated salt is of no importance. Since $c_0 = c_1 = c_2$, it follows for a binary salt that. $c_1c_2 = c_0^2 = K_{sp}$.

* For a salt of any valence type like $A_{\nu_1}B_{\nu_2}$ we have

$$K_{sp} = [\nu_1 A^+]^{\nu_1} \times [\nu_2 B^-]^{\nu_2} = (\nu_1^{\nu_1} \quad \nu_2^{\nu_2}) \quad c_0^{\nu_1+\nu_2},$$

where the brackets enclose the total molar concentration and c_0 is the molar solubility of the salt.

* When the data for the solubility product are critically examined, it is found that the values are not always constant with increasing salt content and that in some cases, notably higher valence electrolytes, the phenomena which in the past has often been erroneously called the repression of the ionization of a salt by a common ion is actually reversed. This is due to the fact that solubility product principle, which is only a special case of the law of mass action, depends upon the applicability of the gas laws when stated in terms of concentration units, and it is clear that the constancy of the solubility product when thus stated is a measure of the applicability of the gas laws. From the considerations given in **149** and **188b, c,** it follows that the law should be obeyed quite exactly by neutral molecules but less so by ions depending primarily upon their valence and the ionic strength of solution.

* Thus, the product for anthracene picrate is constant, but the values for $AgIO_3$, instead of remaining constant, show an increase on the addition of salt which seems to be a perfectly general phenomenon with ions. Recent work has shown that this increase, although small in the case of uniunivalent salts, is enormous with higher-valence salts—27700 per cent in the case of a tritrivalent salt on the addition of 1.0 M $MgSO_4$![1] The effect on the activities of the ions in such cases is so great that the common ion effect is completely obliterated and the solubility actually increases. A good example is the 50 per cent increase in solubility of $La(IO_3)_3$ ($c_0 = 0.001$ M) caused by the addition of 0.1 M $La(NO_3)_3$.[2]

* A general treatment of solubility then must necessarily involve a knowledge of the activities of the ions, and, conversely, by studying the effects of added salts upon the solubility of other salts we have one of the most accurate and simple methods for determining the dependence of the activity coefficient on the concentration. In a saturated solution the activity product of

[1] * BRONSTED and PETERSON, *J. Am. Chem. Soc.*, **43,** 2280 (1921).

[2] * HARKINS and PEARCE, *J. Am. Chem. Soc.* **38,** 2679 (1916).

the ions must equal that of the solid in equilibrium with it or, from the general form of the law of mass action, we have for the salt $A_{\nu_1}\ B_{\nu_2}$

$$(a_{A_{\nu_1}\ B_{\nu_2}})^{\nu_1+\nu_2} = (a_A+)^{\nu_1} \cdot (a_B-)^{\nu_2} = Const. \qquad (206a)$$

and, introducing (193c) $a = c \cdot f$,

$$c_{1^+}^{\ \nu_1} \cdot c_{B^-}^{\ \nu_2} \cdot f_{1^+}^{\ \nu_1} \cdot f_{B^-}^{\ \nu_2} = Const, \qquad (206b)$$

where c is the molar concentration and f the stoichiometric activity coefficient. Since the activity coefficient of the saturating salt f equals

$$f_{1^+}^{\frac{\nu_1}{\nu_1+\nu_2}} \cdot f_{B^-}^{\frac{\nu_2}{\nu_1+\nu_2}} \qquad (cf.\ 193k') \quad (206c)$$

we have

$$K_{sp}^{\frac{1}{\nu_1+\nu_2}} f = Const.\ \text{(rigid)}. \qquad (206d)$$

If, now, we introduce the approximate form of the Brönsted-Debye equation for f (Eq. (193w)), we obtain

$$K_{sp}^{\frac{1}{\nu_1+\nu_2}}\, e^{-3\alpha z_1 z_2 \sqrt{\mu} - 2\beta\mu} = Const. \qquad (206e)$$

as a general statement for the solubility of a salt which is valid to approximately 0 1 to 0 2μ.

* The value of the constant may be defined by the solubility product in pure water $(K_{sp})_0$ which yields the relation

$$\frac{1}{\nu_1 + \nu_2} log_{10} \frac{(K_{sp})}{(K_{sp})_0} = \frac{3\alpha z_1 z_2}{2.303}(\sqrt{\mu} - \sqrt{\mu_0}) + \frac{2\beta}{2.303}(\mu - \mu_0), \quad (206f)$$

where μ_0 is the ionic strength of the saturated solution in water. This equation enables one to calculate the change in the solubility product caused by the addition of foreign electrolytes and from this the molar solubility c_0 of the saturating salt. Although Eqs. (206d and e) have been established for a number of cobaltammine salts of varied valence types and for the salts[1] TlCl, Ag_2SO_4, $AgBrO_3$, $CaSO_4$, it should be noted that there are a few cases where it appears to break down as an exact law; for example, with mixtures of salts of high unsymmetrical valence; the enormous solubility increase of AgCN in KCN solutions is a well-known example of another kind. The classical theory explains this by the formation of a chemical complex for which we have the equilibrium relation

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[1] *Loc. cit.*, 188c.

$$\frac{a_{Ag^+} \cdot a^2_{CN^-}}{a_{Ag(CN)_2^-}} = K_{\text{Instability}} = \text{approx. } 10^{-21}. \tag{206g}$$

*In this case the complex ion behaves as a weak electrolyte, as shown by the magnitude of the constant, a state of affairs which the theory as given above makes no attempt to include. At the present writing it is not clear whether a sharp distinction[1] can always be drawn between the electrostatic complexes of the Bronsted-Debye theory and the complex ions of the classical theory, or whether the chemical complex ion is simply an exaggerated case of the phenomena which Bronsted calls "the specific interaction of the ions."[2]

197. Equilibrium between Two Solutions.—The distribution of benzoic acid between water and benzene may be discussed as an example of an equilibrium between two solutions. Benzoic acid is dissociated into ions in the aqueous layer, especially at low concentrations, while an association to double molecules occurs in benzene, particularly at higher concentrations. Now according to Nernst's distribution law, the ratio of the concentrations of the undissociated and unassociated molecules in both liquids $\frac{c_u}{c_u'}$, is constant and for room temperature:

$$\frac{c_u}{c_u'} = 0.796. \tag{207}$$

Equation (185) states that $c_u = c(1 - \alpha)$, where c represents the total concentration in water, $c = c_u + c_i$ and α *the degree of dissociation*. In a similar way we get $c_u' = c'(1 - \beta)$, in which we understand $\beta\left(= \frac{2c_d'}{c'}\right)$ to be the *degree of association* in benzene; c_d' is the concentration of double molecules. From Eq. (207) it follows that

$$\frac{c_u}{c_u'} = \frac{c(1 - \alpha)}{c'(1 - \beta)} = 0.796 \quad \text{or} \quad \frac{c}{c'} = 0.796\frac{(1 - \beta)}{(1 - \alpha)} \tag{207a}$$

At very *low concentrations* β is very small compared to unity, while α is very nearly equal to unity We can, therefore, put $\alpha = 1$ in the numerator in the L.M.A. $\left(\frac{c_i^2}{c_u} = \frac{\alpha^2 c}{(1 - \alpha)} = K\right)$ and get $(1 - \alpha) = \frac{c}{K}$. By substituting this value and neglecting β in Eq. (207a), it follows that:

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[1] *See **352** for an electrostatic explanation of complex ions.

[2] **J. Am. Chem Soc.*, **44**, 878 (1922), **42**, 782 (1920).

$$\frac{c^2}{c'} = Const. \tag{208}$$

Conversely, at *higher concentrations* α may be disregarded, while β assumes a considerable value; therefore $\beta = 1$ may be substituted in the denominator in the equation of mass action $\left(\frac{c_u'^2}{c_d'} = \frac{2(1-\beta)^2c'}{\beta} = K'\right)$, so that $1 - \beta = \sqrt{\frac{K'}{c'}}$, and hence Eq. (208a) follows from Eq (207a):

$$\frac{c}{\sqrt{c'}} = Const., \tag{208a}$$

an equation which is identical with Eq. (208) except for the numerical value of the constants. In Table 43 the measurements of Hendrixson[1] are evaluated according to Eq (208a); the conditions of application (large β, and small α values) are satisfactorily fulfilled The last column of Table 43 shows that $\frac{(1-\beta)^2c'}{\beta}$ is very nearly constant, as the L M.A. requires for the equilibrium between simple and double molecules within the benzene phase. The region of applicability of Eq (208) is reached at the most minute concentrations for which no measurements exist.

TABLE 43 --DISTRIBUTION OF BENZOIC ACID BETWEEN WATER AND BENZENE AT 10°C[1]

Mole/l aqueous layer	Mole/l benzene layer	α 187	β	$\frac{c}{\sqrt{c'}}$	$\frac{(1-\beta)^2c'}{\beta}$
0.00792	0.0785	0.087	0.8935	0.0260	0.000996
0.00995	0.1461	0.075	0.9210	0.0260	0.000990
0.01155	0.1977	0.069	0.9318	0.0260	0.000987

The distribution ratio of the total concentrations $\frac{c}{c'}$ for dissociated and associated substances is by no means constant, as pointed out in the preceding example, but depends instead upon the state of dissociation or association. Some idea can thus be obtained of the molecular state of a substance in a single solvent from measurements of the distribution ratio $\frac{c}{c'}$, at different concentrations. The simplest limiting cases may be represented by:

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[1] *Z. anorg. Chem*, **13**, 73 (1897).

Equation (207): The molecular weight is equal in both solutions.

Equation (208) or Eq. (208a): The molecular weight is twice as great in one as in the other.

The following example of an equilibrium gas—solid solution, which in principle may be handled as accurately as an equilibrium between several liquid solutions, serves for the application of Eq. (208) to a case where all other molecular-weight measurements fail.

Platinum, and to a still greater extent palladium, possesses the property of absorbing hydrogen in fairly considerable amounts in solid solution. The quantity of hydrogen m taken up by a given amount of palladium has been established experimentally for the different partial pressures p of hydrogen in the gas phase. They give $\frac{m}{\sqrt{p}} = Const.$ Since $m \sim C'$, $p \sim C''$, we arrive directly at Eq. (208) and from this we get the result that the *hydrogen in the solid solution possesses one-half the molecular weight in the gas state or it is predominantly in the monatomic state in the platinum.*[1]

198. Application of Gibbs' Phase Rule to Chemical Systems.

Gibbs' phase rule maintains its validity unchanged for heterogeneous chemical equilibria. Care is required only in fixing the number of components in the system. The minimum number of independent chemical constituents from which the entire system can be formed without the restriction of a quantity ratio between the individual phases constitutes the number of components.

The minimum number in question may be determined most simply by adding together the constituents appearing in the equilibrium and subtracting from this the number of reaction equations determining the equilibrium. Since in every reaction equation the concentration of any one constituent is fixed by the remaining ones as a result of the L.M.A., it can no longer be regarded as independent.

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[1] *This view is confirmed by the study of the crystal structures (see **357**) of the palladium—hydrogen system; McKEEHAN, *Phys. Rev.*, **21**, 334, (1923).

The application of this rule may be explained by some examples:

1. In the dissociation equilibrium of $CaCO_3$ the total number of chemical constituents is 3 ($CaCO_3$, CaO, CO_2), the number of reactions is 1 (Eq. 202*a*)). Accordingly, the number of components is 2. If we attempt to build up the system for one component, namely, $CaCO_3$, then the quantitative relation of the CaO and CO_2 phases is fixed, which is in contradiction to the requirement above. However, the application of Eq. (165) shows that the system is univariant ($P = 3$, $C = 2$, and, accordingly, $F = 1$), which agrees with the result of **195**.

2. Ammonium chloride dissociates into HCl and NH_3 on vaporization. As long as HCl and NH_3 exist in equivalent quantities, $C = 1$, and the system accordingly is univariant. On the other hand, an excess of HCl or NH_3 makes it divariant ($C = 2$, $P = 2$). Now, if we mix solid ammonium chloride powder with solid PbO, then the latter produces a compound $PbOHCl$ with the HCl existing in the vapor, now $C = 3$ (HCl, NH_3, PbO), $P = 4$ (gas, solid NH_4Cl, PbO, $PbOHCl$), and the system is again univariant. The latter example, however, is highly instructive from the standpoint of the law of mass action. Pure ammonium chloride has a very minute vapor pressure (<0.1 *mm.*) at 40°C. and, accordingly, the vapor pressures of NH_3 and HCl are very small. If PbO is added to the system, then the partial pressure of HCl is markedly decreased, owing to the formation of $PbOHCl$, and the partial pressure of ammonia must increase in the same proportion. The total pressure markedly increases, since this increase has a greater influence upon the total pressure than the decrease in the partial pressure of HCl. Designating the total pressure by $2a$ and allowing the HCl to diminish from the value a to $\frac{a}{100}$, then the NH_3 rises to $100a$, and, accordingly, the total pressure increases some fiftyfold. In fact, the pressure over a mixture of ammonium chloride and PbO possesses a pressure of about 1 *atm.* even at 42°C. and, indeed, the gas phase consists of almost pure ammonia!

3. If the four salts KCl, Na_2SO_4, $NaCl$, K_2SO_4 are mixed with one another, a reaction occurs according to the equation

$$2KCl + Na_2SO \leftrightarrows 2NaCl + K_2SO_4.$$

Of course, the conversion proceeds very slowly if only a gas phase is present in addition to the four solid phases. However, a marked acceleration can be produced if the salts are brought into contact with a solvent. Now the phase rule may be used to answer the question whether all four solid salts can coexist under normal circumstances. The number of components here $C = 4 - 1 = 3$, where the presence of a solid is excluded. Provided we are not accidentally concerned with a singular point where the number of degrees of freedom $F = 0$, where pressure and temperature are definitely fixed, the equilibrium will be univariant and therefore a definite pressure will be produced in the gas phase at a definite temperature, *i.e.*, $F = 1$. From Eq. (165) the number of phases capable of existence amounts to $P = C + 2 - F = 3 + 2 - 1 = 4$, of which three are solid phases. From this it follows that one of the solid phases must be completely consumed in the reaction. If we wish the equilibrium to be divariant, then the composition of the solid phases originally present must be so chosen at the start that two of them disappear together in the transformation.

Thus a reaction in a heterogeneous system proceeds to the complete disappearance of an individual reactant so long as these may be represented by separate phases, which is in contrast to the homogeneous reactions where the conversion is always theoretically incomplete.

2. THE THERMODYNAMICS OF CHEMICAL EQUILIBRIA

The chief task of the thermodynamics of chemical equilibria is to calculate from physicothermal data the position of a chemical equilibrium at any temperature when it is inaccessible to direct experimental measurement. The solution of this problem will be our chief concern in the following chapter.

a. Change of Heat Content in Chemical Reactions

199. The Heat of Reaction at Constant Volume and Constant Pressure.—The most striking thermal quantity of a reaction is the change in heat content H, *i.e.*, the quantity of heat which is liberated when a mole of substance is transformed in a reaction. We differentiate between the heat of reaction at constant volume and that at constant pressure. The liberation of heat at constant volume proceeds without the performance of any work and is, therefore, equivalent to the change of internal energy U of the system. But since previously U has been understood to be the increase of internal energy of the system, while a positive change of heat content U' represents an energy decrease, we have

$$U = -U'. \tag{209}$$

The heat content of the reaction at constant pressure H' corresponds to the quantity H (see **27**). However, this still contains the amount of work pv which is necessary to overcome the external pressure p where the volume of the system increases by v and we have, according to Eq (55a),

$$H = U + pv = -H' \tag{209a}$$
$$H' = U' - pv. \tag{209b}$$

Since, in practice, the majority of reactions proceed at constant pressure, we shall, as a rule, use the heat content of reaction H' in what follows. In certain cases, for example, such as combustion in a bomb calorimeter, the experiments, of course, yield values for U'. Therefore it is necessary to determine the quantity pv to convert U' to H'. Whenever one mole of an ideal gas is formed or disappears in the reaction, $pv = \pm RT$. H' can be set as practically equal to U' for reactions which involve only solid and liquid bodies.

200. Hess' Law of Constant Heat Summation.—According to the First Law, the difference in the internal energy which a chemical system possesses before and after a change must be independent of the path by which the change occurs, for, if a difference U_1 is obtained from one path while a difference U_2 is given by another path, then we could obtain the energy $U_1 - U_2$ from nothing by changing the system back and forth upon the two paths. This would constitute a perpetual motion machine of the first class, which is impossible.

This result is synonomous with the **law of constant heat summation** enunciated by Hess in 1840 before the general form of the First Law had been formulated If one time we allow a system to go directly from state 1 to state 2 and at another time through a series of intermediate steps, then the *heat of reaction from the direct change is equal to the sum of the observed heats of reaction for the individual intermediate reactions.* It may easily be proved that this law holds for the heat of reaction at constant volume U' as well as at constant pressure H'.

The burning of carbon may be considered as a simple example to illustrate Hess' law. If a gram-atom of C (diamond) is burned to CO_2 with one mole of O_2, then 94,400 *cal* will be liberated Now if we burn the carbon first to carbon monoxide and this then to carbon dioxide, the heat of reaction for the first case amounts to 26,100 *cal.* and for the second to 68,300 *cal*, or a total of 94,400 *cal.*

Hess' law is of the greatest practical importance for determining a heat of reaction which is not accessible to direct measurement. Although the heat of reaction in forming a compound from its elements, the so-called heat of formation H_F' is of considerable theoretical interest, yet the reaction for the formation of a compound from its elements can rarely or never be carried out directly except with difficulty. On the other hand, it is relatively easy to measure the heats of combustion of numerous compounds. In order to obtain the heat of formation of a compound, the sum of the heats of combustion $\Sigma H_c'$ of the elements contained in the compound as well as the heat of combustion H_c' of the compound, must first be determined Hess' law states that

$$\Sigma H_c' = H_F' + H_c' \quad \text{or} \quad H_F' = \Sigma H_c' - H_c' \qquad (210$$

The application of this equation may be facilitated by means of a simple scheme of calculation. Write down the chemical equations which are to be combined, and put the numerical values of H' on the right side Those symbols appearing in parentheses indicate a negative internal energy of the constituent (the symbols refer to the gas state unless otherwise noted). The First Law or Eq (210) states that the amounts of energy represented by the symbols or numerical values may be added or subtracted as ordinary algebraic quantities

The determination of the heat of formation of benzene vapor may serve as an example of this type of calculation From the heat of combustion of liquid benzene U' in a bomb calorimeter a value of 781,000 *cal* is obtained; however, since 8000 *cal* are absorbed in the vaporization of one mole at constant pressure, H' for gaseous benzene is greater by this amount. The conversion from U' to H' increases this by $^5/_2RT$ = 1500 *cal*, which must be added to U', since in Eq. (209*b*) ν is negative, *i e*, $^5/_2$ moles of gas disappear on burning. Therefore, for gaseous benzene $H'_c = 781{,}000 + 8000 + 1500 = 790{,}500$ *cal*

The following equations hold for the combustion of elementary carbon, hydrogen, and benzene vapor.

$$6(C_{\text{solid}}) + 6(O_2) = 6CO_2 + 6 \times 94{,}400 \textit{ cal} \qquad \text{(I)}$$
$$3(H_2) + {}^3/_2(O_2) = 3(H_2O_{\text{liq}}) + 3 \times 68{,}400 \textit{ cal} \qquad \text{(II)}$$
$$(C_6H_6) + {}^{15}/_2O_2 = 6(CO_2) + 3(H_2O_{\text{liq}}) + 790{,}000 \textit{ cal.} \qquad \text{(III)}$$

Subtracting (III) from the sum of (I) and (II),

$$6(C_{\text{solid}}) + 3(H_2) - (C_6H_6) = -18{,}900 \textit{ cal.}$$
$$6(C_{\text{solid}}) + 3(H_2) = (C_6H_6) - 18{,}900 \textit{ cal.}$$

This gives a *negative heat of formation*, *i e*, heat is absorbed in the formation of benzene from its elements.

We call a reaction which absorbs heat *endothermal*, while a process which gives off heat is designated as *exothermal*. There is no fundamental difference between the two types of reactions, for example, if the formation of benzene is endothermal, the decomposition $(C_6H_6) \rightarrow 6(C_{solid}) + 3(H_2) + 18{,}900$ *cal.* may be represented as an exothermal process, which is identical algebraically with the equation of formation. In order to avoid the possibility of an error in sign, it is expedient to write all reactions so that they appear exothermal.

201. The Temperature Coefficient of the Heat of Reaction (Kirchhoff's Law).—As was first shown by Kirchhoff[1] in 1858, the temperature coefficient of the heat of reaction is closely related to the molecular heat of the reacting substances, and for constant volume:

$$\frac{dU'}{dT} = \sum n_1C_{v_1} - \sum n_2C_{v_2} \tag{211}$$

and for constant pressure:

$$\frac{dH'}{dT} = \sum n_1C_{p_1} - \sum n_2C_{p_2}, \tag{211a}$$

where the expressions $\Sigma n_1C_{v_1}$ and $\Sigma n_1C_{p_1}$ represent the sum of the products of the number of moles and the molecular heats of the initial substances, and $\Sigma n_2C_{v_2}$ and $\Sigma n_2C_{p_2}$ the corresponding sums of the final products. The differences are frequently abbreviated, $\Sigma n_1C_{v_1} - \Sigma n_2C_{v_2}$ to ΣC_v or $\Sigma n_1C_{p_1} - \Sigma n_2C_{p_2}$ to ΣC_p.

To prove Eqs. (211) and (211*a*), assume that the system exists at the temperature T before the conversion and after the conversion at $T + dT$. This change may be carried out over two different paths:

1. Isothermal conversion of the initial substance at the temperature T and heating of the reaction products from T to $T + dT$.

2. Heating the initial substance through an interval of dT and conversion at the temperature $T + dT$.

The first method requires an addition of energy of $-U' + \Sigma n_2C_{v_2}dT$, or $-H' + \Sigma n_2C_{p_2}dT$, depending upon whether the process proceeds at constant volume or at constant pressure.

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[1] The formula derived by Kirchhoff includes the general case in which not only temperature but also the pressure and the volume may change (see the case of heat of vaporization mentioned in **126**).

The addition of energy for the second path correspondingly amounts to

$$+\sum n_1 C_{v_1} dT - \left[U' + \left(\frac{\partial U'}{\partial T}\right)_v dT\right]$$

$$\text{or} \qquad \sum n_1 C_{p_1} dT - \left[H' + \left(\frac{\partial H'}{\partial T}\right)_p dT\right].$$

According to the First Law, both amounts of energy must be the same (the energy difference must be independent of the path), *i e.*, the relations

$$\sum n_2 C_{v_2} dT = \sum n_1 C_{v_1} dT - \left(\frac{\partial U'}{\partial T}\right)_v dT$$

$$\sum n_2 C_{p_2} dT = \sum n_1 C_{p_1} dT - \left(\frac{\partial H'}{\partial T}\right)_p dT$$

are synonymous with Eq. (211) or Eq. (211*a*).

Besides, on the basis of the First Law, Eq (211) may be looked upon as a permissible generalization of Eqs (17) and (17*a*). The absolute value of the internal energy of the entire system before the conversion amounts to U_1 at T, and at $T + dT$ to $U_1 + \left(\frac{\partial U_1}{\partial T}\right)_v dT = U_1 + \Sigma n_1 C_{v_1} dT$, where U_1 is the sum of the internal energies of the individual initial substances and $\frac{\partial U_1}{\partial T}$ is the sum of the molecular heats. At the T the internal energy of the system after the conversion amounts to U_2 and at $T + dT$ to $U_2 + \left(\frac{\partial U_2}{\partial T}\right)_v dT = U_2 + \Sigma n_2 C_{v_2} dT$. Now, according to the First Law, the heat of reaction U' is always equal to the difference of the absolute energies Therefore at T, $U' = U_1 - U_2$, and for $T + dT$, $U' + \frac{\partial U'}{\partial T} dT = U_1 + \Sigma n_1 C_{v_1} dT - U_2 - \Sigma n_2 C_{v_2} dT$, from which Eq. (211) follows directly.

While we may look upon the difference ΣC_v and, therefore, $\frac{dU'}{dT}$ as constant for small temperature differences, and can then apply Eq (211) directly, we must introduce an integration for the calculation of U' or H' over a greater temperature interval, for example, between absolute zero and a given temperature T, namely,

$$U' = U_0' + \int_0^T \sum C_v dT \quad \text{or} \quad H' = H_0' + \int_0^T \sum C_p dT, \tag{212}$$

where the individual values for C_v and C_p are to be represented as functions of the temperature. In addition to the heats of reaction U' and H' at higher temperature, we must possess a knowledge of the temperature curve of the specific heat in the neighborhood of the absolute zero in order to determine the values U_0 and H_0' (heat of reaction at absolute zero).

Since Eq. (212) is of the greatest importance for the calculation of chemical equilibria, let us carry out a numerical evaluation for the formation of ammonia from its elements

$$3(H_2) + (N_2) = 2(NH_3) + 21{,}900\ cal \text{ at } 0°C.$$

The molecular heats of the reacting gases may be accurately represented by the following equations for the temperature interval $T = 273$ to about 1000°.

$$H_2 \cdot C_p = 6.90$$
$$N_2 \cdot C_p = 6.96$$
$$NH_3 . C_p = 8.62 + 0.0007(T - 273) + 5.1 \cdot 10^{-6}(T - 273)^2$$
$$= 8.04 + 0.0007T + 5.1 \cdot 10^{-6}T^2$$

We, therefore, obtain

$$\frac{dH'}{dT} = \sum C_p = 3C_{pH_2} + C_{pN_2} - 2C_{pNH_3} = 11.76 - 0.00014T - 10.2 \cdot 10^{-6}T^2$$

Since this expression is established only for temperatures above 0°C, it cannot be applied for the calculation of the true value of H_0'. However, the extrapolated value of H'_{0e} obtained by means of Eq. (212) suffices, provided the equation is used later only for the higher temperatures. In order to obtain the true value of H_0', the actual temperature curve of the molecular heats must, of course, be accurately determined down to the lowest temperatures.

Since the heat of reaction H'_{273} measured at 273° amounts to 21,900 *cal.*, we obtain:

$$H_{0e}' = 21{,}900 - \int_0^{273}(11.76 - 0.00014T - 10.2 \cdot 10^{-6}T^2)dT$$
$$= 21{,}900 - 3210 + 52 + 68 = 18{,}810\ cal,$$

therefore

$$H'_T = 18{,}810 + 11.58T - 0.0007T^2 - 3.4 \cdot 10^{-6}T^3 \qquad (212a)$$

For a temperature of $T = 932°$ this gives $H'_T = 26{,}410$ *cal*, a value which Haber[1] was able to verify by direct calorimetric measurement.

202. Heat of Reaction and Chemical Equilibria.

—We now approach the solution of the task set forth above; namely, the calculation of a chemical equilibrium from thermal data. Without doubt a reaction *generally* proceeds more "violently" the further the initial mixture is displaced from equilibrium. This appears almost to coincide with the assumption that the magnitude of the heat of reaction is a measure for the violence of the reaction or for its affinity (the Thomsen-Berthelot rule) Hence, from this a given reaction must proceed with a greater heat production the further the system is from the equilibrium point at the beginning of the reaction, and the conversion must result without noticeable heat production in a system which is very nearly in equilibrium at the start. There are numerous simple examples, however, which show that this is by no means the case.

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[1] *Z. Elektrochem.*, **20**, 597 (1914).

If we condense the saturated water vapor existing in equilibrium with liquid water, then we liberate an appreciable amount of heat of condensation In chemical reactions the relations are just the same. In the union of NO_2 to N_2O_4, 6450 *cal* per mole are developed irrespective of whether the NO_2 already exists at the start in equilibrium with the existing N_2O_4 or whether it comes from pure NO_2

Although the heat of reaction alone does not give a direct measure of the position of the chemical equilibrium, nevertheless it offers the most practical means which leads indirectly to a thermodynamic calculation of chemical equilibrium by use of the concept of maximum work.

b. Maximum Available Work

203. General.—In addition to the internal energy U or H, the maximum work $A_{T,p}$ or $A_{T,v}$ (see **27**) proves to be a characteristic quantity for every thermal reaction In contrast to the heat of reaction these quantities, as has been pointed out in **30**, lead directly to the following simple criterion for thermal equilibrium:

$$A_{T,v} = 0 \quad \text{or} \quad A_{T,p} = 0. \qquad (68, 68a)$$

Therefore, *no (useful) work is performed by the conversion of the materials of a chemical system existing in equilibrium.*

When the work performed is positive, the reaction proceeds spontaneously, but when it is negative, it is necessary to supply energy in order to make the reaction proceed. Apart from secondary restrictions, the process becomes more labile the greater the amount of positive maximum work of the process, and therefore the greater the tendency of the system to rearrange itself. As mentioned in **30** the tendency of the components to unite is designated as **affinity** in chemical reactions. It is, therefore, appropriate to *look upon the maximum available work as the exact measure of affinity.*

The task of ascertaining $A_{T,v}$ or $A_{T,p}$ from U or H according to Eqs. (52) or (56) will form the theme of the succeeding chapters. In this we will first consider the relation between the maximum useful work and other physicochemical quantities, which are accessible to direct or indirect experimental determination. As has been emphasized many times before, it is important that the reaction be conducted reversibly if the maximum work is to be obtained

α THE DETERMINATION OF THE MAXIMUM AVAILABLE WORK $A_{T,p}$ BY THE ISOTHERMAL EXPANSION OF GASES OR SOLUTIONS

204. Direct Application of the Fundamental Formula.—A greater part of the methods for the estimation of the maximum work of a process depends upon Eq. (78) which has frequently been used before and which holds for the gaseous as well as for the dissolved state, when put in the following form:

$$A = RTln\frac{p_1}{p_2} = RTln\frac{c_1}{c_2}^{*}\left[= 1.986 \cdot 2.303 \cdot T\, log_{10}\frac{p_1}{p_2}\, cal.\right] \qquad (213)$$

* Whenever the system does not follow the gas laws, corrections must first be made for its deviations, *i.e.*, fugacity and activity replace pressure and concentration in the general case (*cf* **188b**).

The application of Eq. (213) may first be illustrated by the simplest possible example, namely, the reciprocal transition of two allotropic modifications; except for the transition point, both modifications possess different vapor pressures and, indeed, the vapor pressure of the labile modification p_1 must be greater than that of the stable p_2. Now the transition may be carried out through the gaseous state, *i.e.*, we vaporize the labile modification, allow the vapor to expand isothermally from p_2 to p_1, and condense it to the stable modification at the pressure p_1. Now the work per mole performed in the vaporization is $pv = RT$ and the same quantity is obtained on condensation; therefore, all the work performed is confined to the expansion of the vapor from p_1 to p_2, *i.e.*, the total maximum available work of transition

may be simply represented by Eq. (213) if p_1 and p_2 represent the vapor pressures or c_1 and c_2 the saturation concentrations of both modifications in any solvent.

The measurement of the latter may be carried out for the two modifications of sulfur (rhombic and monoclinic) in some solvent and leads to the results reproduced in the following table[1]

TABLE 44.—THE FREE ENERGY OF THE TRANSITION OF THE TWO MODIFICATIONS OF SULFUR

Solvent	T	c_2 Rhombic sulfur	c_1 Monoclinic sulfur	$-A_{T,p} = RT\ln\frac{c_2}{c_1}$ [*cal* per Mole *S*[1]]
Chloroform	273 2	0 0788	0 1101	−182
Chloroform	288 5	0 1253	0 1658	−161
Benzene	291 6	0 1512	0 2001	−161 5
Benzene	298 3	0 1835	0 2335	−143
	368 4	transition point $c_1 = c_2$		0

[1] Sulfur is dissolved in the octoatomic state in the liquids quoted

Equation (213) is directly applicable for the estimation of the maximum work when a salt takes up water of crystallization. The absorption of the water of crystallization may be considered as being performed so that, instead of presenting the liquid water directly to the anhydrous salt, the water is first vaporized, then the vapor allowed to expand until it has reached the partial pressure of the hydrated salt, and finally it is combined with the salt by condensation. In the expression (Eq. (213)) for the maximum work of the reaction, p_1 therefore represents the saturation pressure of pure water and p_2 the partial pressure of water vapor over the hydrated salt. Siggel (*Z Elektrochem.*, **19**, 340 (1913)) found, for example, that $p_2 = 1.325 \times 10^{-3}$ *mm.* for the partial pressure of the water over $CuSO_4.H_2O$ by extrapolation of the measurements at higher temperatures to $T = 273°$. Since the vapor pressure of pure water at the same temperature amounts to 4.58 *mm.*, then $(A)_{T,p} = 4.571 \; 273 \; \log \frac{4.58}{1.325 \; 10^{-3}} = 4415$ *cal.*

A point at which $(A)_{T,p} = 0$, i e, where pure water and the hydrated salt exist in equilibrium with one another, obviously does not exist in this case

205. Maximum Work of a Gas Reaction.

—The determination of the maximum work which can be obtained from a gas reaction likewise depends directly upon Eq. (213). For simplicity of calculation, a concrete example may be considered, such as the union of hydrogen and nitrogen to form ammonia. We have a relatively large supply of H_2, N_2, and NH_3 in three separate containers with partial pressures amounting to p_{H_2}, p_{N_2}, and p_{NH_3}. In addition to the separate vessels, we have an equilibrium chamber in which this chemical reaction proceeds and in which a large quantity of substance is to be in equilibrium with the partial pressures p'_{H_2}, p'_{N_2}, p'_{NH_3} in the presence of a catalyzer.

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[1] BRONSTED, J. N, *Z. physik. Chem*, **55**, 371 (1906).

Now it is to be assumed that $3dn$ moles of H_2 are converted, with dn moles of N_2, to form $2dn$ moles of ammonia (the initial partial pressures remaining practically unchanged owing to the minute quantity converted). As a rule, the initial pressures differ from the equilibrium pressures and therefore we cannot allow the gases simply to flow directly into the equilibrium chamber, since this would be an irreversible process. In order to bring the latter reversibly from the stock vessels to the equilibrium chamber, we may first expand a requisite quantity of the initial gases for the intended conversion isothermally and infinitely slowly from the initial pressure to that of the equilibrium pressure. We obtain, then, the following amounts of work:[1]

$$H_2: d(A_1)_{T,p} = 3dn\, RT\, ln \frac{p_{H_2}}{p'_{H_2}} \qquad (213a)$$

$$N_2: d(A_2)_{T,p} = dn\, RT\, ln \frac{p_{N_2}}{p'_{N_2}}. \qquad (213b)$$

The gases under the pressures p'_{H_2} and p'_{N_2} may now be transferred reversibly into the equilibrium chamber, using, if necessary, a semipermeable partition. There they react with one another and produce $2dn$ moles NH_3 without exerting a noticeable displacement of the equilibrium and of the partial pressure p'_{NH_3}. We separate the minute excess of ammonia which has been formed, if necessary, by a semipermeable partition, compress it from p'_{NH_3} to p_{NH_3} and then lead it under a pressure of p_{NH_3}

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[1] In case $d(A)_{T,v}$ is determined first, we must take into consideration that the work $3dnp_{H_2}v = 3dnRT$, etc. is still to be performed, in order to bring the gas from the storage chamber into the expansion cylinder. In the transformation to $A_{T,p}$ these quantities are again eliminated on the basis of Eq. (53a).

to the stock vessel. The work performed upon the system in this compression is

$$d(A_3)_{T,p} = 2dn\,RT\,ln\frac{p_{NH_3}}{p'_{NH_3}}\,, \tag{213c}$$

so that it has an opposite sign compared to Eqs. (213*a*) and (213*b*)

Now for the sum of the work terms Eqs. (213*a*), (213*b*) and (213*c*) we get

$$dA_{T,p} = 3dn\,RT\,ln\frac{p_{H_2}}{p'_{H_2}} + dn\,RT\,ln\frac{p_{N_2}}{p'_{N_2}} - 2dn\,RT\,ln\frac{p_{NH_3}}{p'_{NH_3}}$$

or

$$dA_{T,p} = dn\,RT\left\{ln\frac{p^3_{H_2}p_{N_2}}{p^2_{NH_3}} - ln\frac{p'^3_{H_2}p'_{N_2}}{p'^2_{NH_3}}\right\} \tag{214}$$

Since according to the fundamental law previously emphasized, the quantity $A_{T,p}$ does not change during a conversion in the equilibrium chamber, no work is performed Therefore, Eq. (214) represents the maximum available work $A_{T,p}$ to be obtained from the entire process. No assumptions of any kind were made regarding the partial pressures p'_{H_2}, etc in the equilibrium chamber and we can therefore dispose of them as we choose

For example, we may imagine the presence of a second equilibrium chamber, in which the pressures p''_{H_2}, p''_{N_2}, p''_{NH_3} prevail Now let us decompose the ammonia formed completely back to its elements by the use of this second equilibrium chamber, so that the work employed here obviously amounts to

$$dA'_{T,p} = -dn\,RT\left\{ln\frac{p^3_{H_2}p_{N_2}}{p^2_{NH_3}} - ln\frac{p''^3_{H_2}p''_{N_2}}{p''^2_{NH_3}}\right\}.$$

The system has again returned to its initial state.

But for such a case the Second Law (impossibility of a *perpetuum mobile* of the second class) requires that no heat can be transformed into work, so that $dA_{T,p} + dA'_{T,p} = 0$. This equation for the equilibrium pressures leads to the condition that·

$$\frac{p'^3_{H_2}p'_{N_2}}{p'^2_{NH_3}} = \frac{p''^3_{H_2}p''_{N_2}}{p''^2_{NH_3}}.$$

Obviously then, the latter will be fulfilled if any other given partial pressure is choosen such as p'''_{H_2}, etc From this it follows that the expression $\frac{p'^3_{H_2}p'_{N_2}}{p'^2_{NH_3}}$ must always be equal to a constant K_p. *We arrive at the law of mass action in this manner and the latter proves to be a thermodynamic consequence of the Second Law.* But at the same time it presupposes the validity of the gas laws for the reacting substances, as we observe from the application of Eq. (213).

In case Eq. (214) is applied to the conversion of *one mole* ($dn = 1$) of a given gas reaction, which proceeds according to the scheme $nA + mB + \ldots = qA' + pB' \ldots$, and at the same time the constant of the L M.A. K_p is introduced the result is, finally:

$$A_{T,p} = RT\left(ln \frac{p^n{}_A p^m{}_B \cdots}{p^q{}_{A'} p^r{}_{B'} \cdots} - lnK_p\right) \qquad (214a)$$

We can also use concentrations instead of partial pressures in Eq. (213) and in this manner the following equivalent expression is arrived at:

$$A_{T,p} = RT\left(ln \frac{[A]^n[B]^m \cdots}{[A']^q[B']^p \cdots} - lnK_c\right). \qquad (214b)$$

in which the concentrations and K_c appear instead of the partial pressures and K_p in Eq. (214*a*).

A numerical calculation of the maximum available work, according to Eq. (214*a*), may be represented by an example of the formation of NH_3. If all the initial and final partial pressures (p_{H_2}, p_{N_2} and p_{NH_3}) are made equal to 1 *atm*, then

$$A_{T,p} = -4.571\ T\ log_{10} K_p\ cal. \qquad (214c)$$

from which the values given in Table 45 are obtained. It should be noted that the maximum work $(A)_{T,p}$ is negative for this reaction.

TABLE 45

T	$log_{10} K_p$	$A_{T,p}$(*cal* per 2 moles NH_3)
773°	4.81	−17000
995	6.46	−29400
1187	7.44	−40350

Although the formation of ammonia represents an exothermal reaction, the latter does not proceed spontaneously under the conditions of equal pressure for all components, but, instead, an appreciable quantity of work must be performed upon the system in order to bring about a union of the elements, especially at higher temperatures.

This result is clear even without Eq. (214c). When equilibrium is established, the NH_3, coming from the pressures $p_{H_2} = p_{N_2} = p_{NH_3} = 1$, disappears, since the constant K_p is greater than unity, *i.e.*, a decomposition and not a formation ensues spontaneously. If, on the other hand, the initial concentrations of H_2 and of N_2 are increased and that of the NH_3 decreased so far that the expression $\frac{p^3_{H_2} p_{N_2}}{p^2_{NH_3}}$ is greater than K_p, we obtain a positive value for $A_{T,p}$, according to Eq. (214a), *i.e.*, ammonia formation proceeds spontaneously.

206. Maximum Work $A_{T,p}$ of Heterogeneous Reactions.— We obtain Eq. (214a) for the maximum available work of a chemical reaction whose components are partly solid (or liquid) and partly gaseous. However, the pressures of those components disappear when the components are present in the initial or final states, as well as at equilibrium as solid bodies, for, owing to the presence of solid bodies, the partial pressures of these substances have a constant value in the equilibrium chamber just as in the initial mixture. Thus, an expansion which involves the performance of work is impossible in this case.

As an example (for a univariant system), let us again consider the formation of calcium carbonate from carbon dioxide and calcium oxide. Equation (214a) reduces to

$$A_{T,p} = RT(ln\, p_{CO_2} - ln\, p'_{CO_2}), \qquad (214d)$$

since in the presence of solid carbonate and of oxide

$$p_{CaCO_3} = p'_{CaCO_3} \quad \text{and} \quad p_{CaO} = p'_{CaO}.$$

Solid carbon dioxide, however, separates at very low temperatures and sufficiently high values of p_{CO_2}. In this case the vapor pressure of solid carbon dioxide is to be inserted for p_{CO_2} in Eq. (214d). The rule that the partial pressure of every substance which exists as a solid body drops out in the expression for the maximum work is obviously not impaired by this, since the solid carbon dioxide is capable of existence only outside the equilibrium chamber, while within the same only two solid phases can persist according to the phase rule (except for a singular point where $A_{T,p}$ disappears).

The system carbon (solid), oxygen, carbon dioxide serves as an example of a two-component system with only one solid phase and one gas phase and which is, therefore, divariant in its equilibrium. For the ratio of equilibrium pressures $K = \frac{p''_{O_2}}{p''_{CO_2}}$ we found the value $10^{-15.62}$ for T = 1300° in **196**. It follows from this that $A_{T,p}$ = 92700 *cal.* at T = 1300°, in case the partial pressures of the oxygen existing at the start and of the CO_2 formed are equal $\left(\frac{p_{O_2}}{p_{CO_2}} = 1\right)$. In the combustion of carbon, $A_{T,p}$ depends but little on the temperature, since *log K* is inversely proportional to T (see **227**) and therefore we obtain a value for room temperature which is only a few per cent different from that at 1300°. The change of heat content of the reaction amounts to 94400 *cal* (diamond), which is very nearly the same value as for the maximum work, *i e*, it is just in this case of the combustion of carbon to carbon dioxide that we may extract almost the theoretical quantity of internal energy as maximum work, while sometimes in other cases, for example, the NH_3 equilibrium, H' and $A_{T,p}$ do not agree even in sign.

β. ESTIMATION OF THE MAXIMUM AVAILABLE WORK THROUGH MEASUREMENTS OF ELECTROMOTIVE FORCE (E M F)

207. The E.m.f. as a Measure of Maximum Work.—When it is possible to construct a reversible galvanic element the *e m f.* serves as a measure of the maximum work of the reaction yielding the current. This is possible in most reactions in which metals appear in the elementary state as well as in some gas reactions. The reaction

$$Pb + 2AgCl_{(solid)} = 2Ag + PbCl_{2(solid)} \qquad (215)$$

serves as an example of a reaction which qualifies for the preparation of a reversible galvanic element. If a lead electrode is covered with solid lead chloride and a silver electrode with silver chloride and both are dipped in a potassium chloride solution of any concentration, they show an electrical *potential difference E* which may, as a rule, be designated as the *electromotive force* (*e m f*) of the cell.

If the two electrodes are connected with a wire, a current flows from the silver to the lead electrode, owing to the *e m f.* The following reactions take place within the element: the metallic lead dissolves as Pb^{++} ions which unite with the chloride ions of the KCl as $PbCl_2$ Metallic silver plates out on the silver electrode through discharge of the Ag^+ ions by which a definite quantity of chloride ions are liberated. Inasmuch as chloride ions are bound at the lead electrode and freed at the silver electrode, they migrate back through the solution and carry with them a definite quantity of electricity, so that a negative current flows from the silver pole to the lead pole within the cell, *i.e.*, a positive current flows in the reverse direction. As long as the element yields a current, a conversion occurs according to Eq. (215).

Now we could use the *e m f.* of the element for the performance of work by means of an electric motor. In order to achieve the maximum available work, the element must be permitted to work reversibly, *i e*, only a very minute current is allowed to flow, so that the equilibrium of the substances within the element is not markedly disturbed. If too great a current is drawn from the cell, the chloride ions do not have sufficient time to become compensated. The element then works irreversibly, as is shown by a fall of the original *e.m f.*

If we allow the element to work so long that a mole of lead is displaced (= 2 gram-equivalents of silver), the electrical work performed which is equivalent to the maximum available work amounts to

$$A_{T,p} = 2\mathfrak{F}E, \tag{216}$$

since 2 $\mathfrak{F}$ of electricity are combined with one mole of lead or 2 gram-equivalents of silver For a process in which n_e equivalents are converted and therefore which forms an n_e-valent ion, we obtain, instead of Eq (216), the general form

$$A_{T,p} = n_e\mathfrak{F}E. \tag{216a}$$

If we express the *e m f* in the usual electrical units (volts) but desire to obtain the maximum work in calories, then we must set (compare Table 1)

$$A_{T,p} = n_e \frac{96,500}{4.187}E = n_e 23,050E\ cal. \tag{216b}$$

Since the *e.m f.* of the lead chloride-silver chloride element is estimated at 0.4889 *volts* at room temperature, the maximum available work in the conversion of one mole of lead in Eq. (215) amounts to 22,540 *cal.* in calorimetric units.

Elements which depend upon reactions of the scheme of Eq. (215) are distinguished in many cases by the excellent reproducibility of their *e.m f.* They are, therefore, qualified for use as standard elements (such as calibrating voltmeters and the like).

One of the best-known standard elements—the so-called **Clark cell**—depends upon the reaction:

$$Zn + Hg_2SO_{4(solid)} + 7H_2O = ZnSO_4.7H_2O_{(solid)} + 2Hg.$$

The reciprocal transition of two allotropic modifications of a metal, such as tin, furnishes an instructive example for the determination of the maximum work of a chemical reaction from the *e.m.f.* of a galvanic element. We prepare an electrode of gray tin and another of white tin; as a solution we will use a liquid containing tin ions.

The exact measurements of such a tin cell encounters certain (secondary) experimental difficulties, but yet at a temperature under 18° the current flows so that white tin is dissolved and gray tin is formed, while at higher temperatures the *e.m.f.*, is reversed. The *e.m.f.* of the cell is equal to zero at 18°, and according to Eq. (216) the maximum work $A_{T,p}$ also disappears, so that the system must be in equilibrium on the basis of Eq. (68*a*). Even without Eq. (68*a*) it is clearly seen that both modifications are in equilibrium at 18° (*the transition point*), since a disappearance of the *e.m.f.* is equivalent to the cessation of the reciprocal transition.

208. The Fuel Cell.—The direct extraction of the available energy of a chemical reaction in the form of electrical energy is not only of theoretical interest but also of far-reaching practical importance. For example, if it were possible to make the energy of the burning of coal, *i.e.*, the reaction $C + O_2 = CO_2$, directly available as an electromotive force,[1] then we could hope to extract the maximum work of a reaction; in this case it is very nearly equal to the change of heat content (see **206**). With the usual heat engine it is possible to convert only a small fraction, at the most about one-third, of the internal energy into mechanical energy. The problem of constructing a practical working fuel cell has been attacked in different ways, though as yet no serviceable solution has been found. In the first place the difficulty lies in the fact that carbon at ordinary temperatures is very non-reactive. Although we can construct a serviceable element by using a molten salt as electrolyte, its establishment, aside from great initial cost, etc., would be uneconomical, since great quantities of energy are consumed in the continuous heating.[2]

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[1] Such an element must possess an *e.m.f.* very nearly equal to 1 *volt* according to Eq. (216*b*), since from **206** $A_{T,p}$ amounts to 92700 *cal.* and $n_e = 4$. (Carbon is tetravalent.)

[2] BAUR, TREADWELL, and TRÜMPLER (*Z. Elektrochem.*, **27**, 199 (1921)) have made exhaustive experimental studies in which they have realized practical fuel cells. References to older literature are given here.* See also RIDEAL and EVANS, *Trans. Faraday Soc.* (1921).

209. The Resolution of the E.m.f. of a Galvanic Cell into Single Potentials.—If one sheet of silver is dipped in a dilute $AgNO_3$ solution and another in a concentrated $AgNO_3$ solution and the solutions are brought in contact with one another, a galvanic element is likewise obtained which differs from the elements hitherto considered in that the electrodes are alike but the solutions into which they are submerged are of different concentrations; such a cell is called a **concentration cell.** A chemical reaction cannot be the reason for the *e.m.f.* in this case; it can only be due to the tendency of the concentrated solution to expand. Therefore, the measurement of the *e.m.f.* of such a concentration cell also leads to a knowledge of the work of expansion of the solutions concerned; this, in turn, gives a method for the determination of unknown ionic concentrations (**183e**).

A method of deriving the formula for a cell of the type

$$\begin{array}{c|c|cc}
\text{Ag} & \text{AgNO}_3\text{ Solution 1} & \text{AgNO}_3\text{ Solution 2} & \text{Ag} \\
 & \text{concentrated} & \text{dilute} & \\
 & c_1 & c_2 & \\
\end{array}$$

$$\text{I} \qquad\qquad\qquad \text{II} \qquad\qquad\qquad \text{III}$$

follows from a consideration of the origin of the *e.m.f.* in the cell. Since no electrical potential difference can appear within a homogeneous[1] phase, we must look for the origin of the *e.m.f.* in the surfaces of the different phases, *i.e.*, a potential difference will be formed at the interfaces. We are concerned with the following:

1. Metal—Solution
2. Solution 1—Solution 2.
3. Solution 2—Metal.

It appears, in general, that all three interfaces contribute in a noticeable way to the total *e.m.f.*

210. Liquid Junction Potentials.—The determination of the potential difference between the two solutions is important. It may be explained *qualitatively* as follows:

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[1] Chemical homogeneity alone is not sufficient, for certain metal electrodes, such as copper, often show different potentials if one portion has been given special treatments, such as electrical deposition, hammering, rolling, polishing, and annealing.

The osmotic pressure drives the positive and negative ions of the concentrated solution into the dilute solution. In case the migration velocities of the two ions are unequal, one ionic species attempts to hasten ahead of the other, but, since the ions are oppositely charged, a very great potential difference would develop if complete separation occurred Therefore, the ions separate only so far that the forces of electrical origin suffice to hinder the faster ion somewhat and accelerate the slower ion a little, so that both ions migrate finally with an equal velocity Now the quantitative application of this consideration leads directly to an equation which permits us to determine the magnitude of the electrical force formed by the diffusion process and therefore also the potential difference between both solutions from experimental data.

Equation (28a) again forms the basis of the calculation $V = \frac{\mathfrak{K}}{f}$

We will consider a volume element of length dx in a cylindrical vessel of cross-section q and, therefore, of volume qdx, the number of ions of one kind present amounts to N' Then the molar concentration in this volume element is given by

$$c = \frac{N'}{\mathbf{N}qdx} \tag{217}$$

The force $\mathfrak{K}$ upon the N' ions is composed

1. Of the force of osmotic pressure, this amounts to $qd\Pi$ for either ion, where $d\Pi$ represents the increase of osmotic pressure for the distance dx

2 Of the electrical force acting in opposite directions, on both ions, occasioned by the diffusion as pictured above. The latter is equal to the unknown strength of the field $\frac{dE}{dx}$ multiplied by the charge of N' ions, which amounts to $N'n_e\frac{\mathfrak{F}}{\mathbf{N}}$. Therefore, we have in total

$$\mathfrak{K}_{N'} = qd\,\Pi \pm \frac{N'n_e\mathfrak{F}}{\mathbf{N}}\frac{dE}{dx}$$

The frictional force of the individual ions may be expressed according to Eq (186) in terms of the mobility U^+ and U^-, the frictional force $f_{N'}$ which is effective for N' ions amounts therefore to

$$f_{N'} = \frac{\mathfrak{F}N'}{U^+\mathbf{N}} \quad \text{or} \quad \frac{\mathfrak{F}N'}{U^-\mathbf{N}}.$$

For the velocity which the ions assume on diffusion we obtain by considering Eq (217)

$$\text{Cation.} \qquad V_0^+ = \frac{U^+}{\mathfrak{F}n_e}\left(\frac{\mathbf{N}qd\Pi}{N'} + n_e\mathfrak{F}\frac{dE}{dx}\right) = \frac{U^+}{\mathfrak{F}n_e}\left(\frac{1}{c}\frac{d\Pi}{dx} + n_e\mathfrak{F}\frac{dE}{dx}\right)$$

$$\text{Anion:} \qquad V_0^- = \frac{U^-}{\mathfrak{F}n_e}\left(\frac{\mathbf{N}qd\Pi}{N'} - n_e\mathfrak{F}\frac{dE}{dx}\right) = \frac{U^-}{\mathfrak{F}n_e}\left(\frac{1\,d\Pi}{dx} - n_e\mathfrak{F}\frac{dE}{dx}\right).$$

Since the ions can be separated from one another only to a very minute degree, V_0^+ and V_0^- must be equal to one another. From this it follows, in case both ions are of equal valence, if we substitute the concentration in place of the osmotic pressures according to Eq (140), that

$$n_e\mathfrak{F}\frac{dE}{dx} = -\frac{U^+ - U^-}{U^+ + U^-}\frac{1}{c}\frac{d\Pi}{dx}$$

$$n_e\mathfrak{F}\frac{dE}{dx} = -\frac{U^+ - U^-}{U^+ + U^-}\frac{RT}{c}\frac{dc}{dx}$$

Since the quantity dx may be eliminated, we obtain on integrating

$$E_{1,2} = -\frac{U^+ - U^-}{U^+ + U^-}\cdot\frac{RT}{n_e\mathfrak{F}}\ln\frac{c_1}{c_2} = \frac{U^+ - U^-}{U^+ + U^-}\cdot\frac{RT}{n_e\mathfrak{F}}\ln\frac{c_2}{c_1}$$

for the potential difference between the concentrated c_1 and the dilute c_2 solution, or by substitution of numerical values for R (electrical units) and $\mathfrak{F}$ as well as introducing decadic logarithms we get:

$$E_{1,2} = \frac{U^+ - U^-}{U^+ + U^-}\cdot\frac{1.983\cdot 10^{-4}}{n_e}\cdot T\log_{10}\frac{c_2}{c_1} \qquad (218)$$

Accordingly, the concentrated solution is negatively charged if $U^+ > U^-$, *i.e.*, if the cation precedes the anion.

If we place two different solutions of any given concentration next to one another, the basis of the calculation remains the same as above, though it leads to considerably more complicated results[1] particularly since the quantity dx cannot always be eliminated, *i.e.*, the potential difference depends not only upon the concentration c_1 and c_2 but also upon the nature of the boundary between the two solutions

In order to avoid the troublesome and frequently uncertain calculation of the boundary potential between two different liquids which, as a rule only plays the rôle of a correction term, it is expedient to eliminate it by experimental precautions. This is most simply accomplished by connecting the two solutions with one another by means of a siphon which is filled with a concentrated solution of KCl or NH_4NO_3,[2] instead of allowing them to touch one another directly.

211. Potential Difference Metal-solution.

—The occurrence of a potential difference at the interface metal-solution was pictured by Nernst (1889) as follows

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[1] See Planck, M., *Wied Ann*, **40**, 561 (1890), Jahn, H., "Grundriss der Elektrochemie," **2** (1905), Henderson, *Z. physik. Chem*, **59**, 118 (1907), **63**, 325 (1908) * Fales and Vosburgh, *J. Am Chem. Soc.*, **40**, 1291 (1918), MacInnes and Yeh, *J. Am. Chem. Soc*, **43**, 2563 (1921).

[2] The efficiency of this device depends upon the fact that the K^+ and Cl^- ions as well as the NH_4^+ and NO_3^- ions migrate at approximately the same speed, so that $U^+ = U^-$ and, therefore, according to Eq. (218), no noticeable potential difference originates at the surface of contact of the siphon liquid and with the relatively dilute (assumed) solutions 1 and 2. (See Bjerrum, N., *Z. Electrochem.*, **17**, 58, 389 (1911).)

The metal has a definite tendency to pass over into the ionic state. It sends a number of positive metallic ions into the solution and therefore assumes a positive charge; hence an electrical double layer (Fig. 52, (*a*)) exists at the interface metal-solution, the formation of which opposes any further solution of positive ions. The formation of the double layer in solution involves, however, only an extremely minute quantity of ions, and measurable quantities of metal dissolve only when the resulting electrical charge is continuously destroyed. We designate this tendency of the metal to go into solution as ions as "**electrolytic solution tension.**"[1]

On the other hand, the ions have a tendency to leave the solution, owing to their osmotic pressure, and to pass over to the metallic state. This tendency is greater the higher the concentration. The electrolytic solution tension of the metal and the osmotic pressure of the ions work against one another. The latter influence predominates with the noble metals, so that a minute quantity of ions is precipitated upon the metal and the latter becomes positively charged while the solution remains negative (Fig. 52*b*). It is only when the electrolytic solution

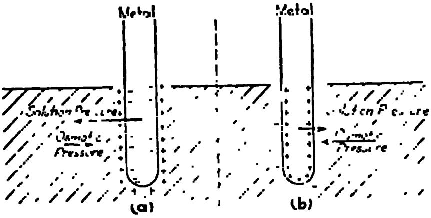

FIG 52

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[1] The real reason for the electrolytic solution tension can only be sought in the existence of an attractive force between the molecules of the solvent and the ions of the metal. It is to be observed that, according to the modern conception of the metallic state, the majority of the atoms are ionized even in the metals (see **370**). The essential reaction in the electrolytic dissolution of a metal consists, therefore, in a hydration of these ions.

* LANGMUIR (*Trans. Am. Electrochem. Soc.*, **29**, 132 (1916)), believes that the source of the potential difference can be explained more satisfactorily upon the basis of the Volta effect (the tendency of metals to lose electrons at the surface of contact) than upon the basis of Nernst's solution pressure concept. BUTLER (*Trans. Faraday Soc.*, **19**, 729 (1924)) considers the Nernst concept kinetically and considers it adequate.

tension and the osmotic pressure of the ions just compensate one another that a zero potential difference prevails between metal and solution.

Since we can vary the fugacity (osmotic pressure)[1] of a given ion, let us specify *an ionic activity for every metal* A_0 for which the solution tension will be abolished and, therefore, the potential difference between the metal and solution becomes equal to zero. We can look upon this characteristic ionic activity as a measure of the solution tension of the metal. The greater we must make this ionic activity the greater is the solution tension of the metal.

In order to obtain a relation between the difference of potential E at the interface metal-solution, the equilibrium activity A_0 and a given activity a, we will consider two metal electrodes (I and II) of the same material submerged in solutions of activity A_0 (I) and of activity a (II) and both solutions are connected so that no liquid junction potential exists. Now a reversible dilution of 1-gram-ion of solution A_0 to an activity a can be followed in two ways: First, let us expand the gram-ion isothermally from an activity A_0 to a; the work performed amounts to $A_1 = RTln\frac{A_0}{a}$. On the other hand, we can dissolve a mole as ions at electrode II and allow the same quantity of ions to be plated out on electrode I whereby the quantity of electricity $n_e\mathfrak{F}$ combined with this quantity of ions falls from the potential of electrode I to the potential II. The electrical work extracted amounts to $A_2 = En_e\mathfrak{F}$, where E is the potential difference between I and II. From the second law, $A_1 = A_2$, *i.e.*,

$$En_e\mathfrak{F} = RTln\frac{A_0}{a}$$

or

$$E = \frac{RT}{n_e\mathfrak{F}}ln\frac{A_0}{a} = \frac{1.983 \cdot 10^{-4}}{n_e}T\,log_{10}\frac{A_0}{a} = -\frac{1.983 \cdot 10^{-4}}{n_e}T\,log_{10}\frac{a}{A_0}. \tag{219}$$

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[1]* In order to conform with the treatment given in (**188b, c** and **191**) the translators have replaced the author's terms of osmotic pressures of the ions and concentrations of the ions in what follows by the terms fugacity of the ions and activities of the ions. The substitution was not made in (**210**), because it seemed best to use the term concentration for developments which are not purely thermodynamic.

Therefore, electrode I, which has the same potential as that of the two solutions, becomes positively charged and electrode II, which dips in solution a, becomes negatively charged. If $a < A_0$ and the ions are positively charged, Eq. (219) indicates the difference of potential, *solution* (a)—*electrode*, for positively charged ions and the potential difference, *electrode—solution* (a), with negatively charged ions. We write therefore

$$E = + \frac{1.983 \cdot 10^{-4}}{n_e} T \log \frac{a}{A_0}. \tag{219a}$$

This equation is valid for the potential difference electrode-solution with positively charged ions and the potential difference solution-electrode for negatively charged ions.

212. E.m.f. of Concentration Cells.—Concentration cells of the type quoted in **209** yield the value of the *e.m.f.* directly. We obtain, by addition of relations, Eqs. (218) and (219) determining the potential differences, I, II, and III if we proceed from the electrode dipping in the concentrated solution a_1

$$E = \frac{1.983 \cdot 10^{-4}}{n_e} T \left\{ \log \frac{a_1}{A_0} - \frac{U^+ - U^-}{U^+ + U^-} \log \frac{a_1}{a_2} + \log \frac{A_0}{a_2} \right\}$$
$$= \frac{1.983 \cdot 10^{-4}}{n_e} T \frac{2U^-}{U^+ + U^-} \log \frac{a_1}{a_2}. \tag{220}$$

Where potential II is suppressed, we obtain

$$E = \frac{1.983 \cdot 10^{-4} T}{n_e} \left\{ \log \frac{a_1}{A_0} + \log \frac{A_0}{a_2} \right\} = \frac{1.983 \cdot 10^{-4}}{n_e} T \log_{10} \frac{a_1}{a_2} \text{ volt} \tag{221}$$

The expression $\frac{1.983 \cdot 10^{-4}}{n_e} T$ assumes the value 0.058 *volt* for $T = 293°$ and univalent ions. Therefore, when we employ two solutions of univalent ions against one another having activities which differ by a power of ten $\left(\log_{10} \frac{a_1}{a_2} = 1\right)$, then the *e.m.f.* of the cell amounts to 0.058 *volt;* for a difference of two powers of ten we obtain 2 × 0.058 *volt*, etc.

213. Electrodes of the Second Type.—When a metallic electrode, such as silver, is coated with a difficultly soluble salt such as AgCl, the silver-ion concentration determines the potential difference at the interface metal-solution, just as above. But in this case the silver concentration is determined solely by the solubility product K_{sp} (see **196**) and the activities of the chloride ions, i.e., we obtain in place of Eq. (219*a*)

$$E = 1.983 \cdot 10^{-4}\, T \log_{10} \frac{K_{sp}}{A_0 \cdot a_{Cl}}$$

If we combine two such electrodes dipping in solutions of different chloride-ion concentrations, then, when the liquid junction potential is omitted, we obtain

$$E = 1.983 \cdot 10^{-4} T \log \frac{[a_{Cl^-}]_2}{[a_{Cl^-}]_1} = -1.983 \cdot 10^{-4} T \log \frac{[a_{Cl^-}]_1}{[a_{Cl^-}]_2} \quad (221a)$$

The same formula holds here (if signs are disregarded) as for electrodes which dip in unsaturated solutions of their own ions. We frequently call the latter **electrodes of the first class**; the designation **electrodes of the second class** is usually made for a metal which is covered with a difficultly soluble salt of the same metal and whose potential depends upon the concentration of the anions of the difficultly soluble salt in solution.

Inasmuch as such electrodes are easy to reproduce, they are frequently employed as standard electrodes, i.e., as the pole opposing the unknown electrode whose potential is to be measured. The normal calomel electrode is frequently used, i.e., mercury, which is covered with calomel and a normal potassium chloride solution.[1]

The potential difference of this electrode against the normal hydrogen electrode (see below) amounts to 0.286 *volt*.

214. Potential Series of the Elements.—When we combine different electrodes with each other, such as a copper electrode in a Cu^{++} ion solution with a zinc electrode in a Zn^{++} solution or a so-called Daniell cell, the term A_0 which is proportional to the solution tension is not eliminated, and we therefore obtain apart from the potential difference at the boundary of the two liquids the sum of the potential differences Cu/Cu^{++} and Zn^{++}/Zn for the *e.m.f.* of the cell. According to Eq. (219) when we keep the signs in mind this gives

$$E = \frac{1.983 \cdot 10^{-4}}{2} T \left(\log \frac{a_{Cu^{++}}}{A_{0Cu^{++}}} - \log \frac{a_{Zn^{++}}}{A_{0Zn^{++}}} \right) \qquad (222)$$

---

[1] * Lately, the saturated KCl calomel cell has come into extensive use in this country, owing to the ease with which a definite concentration may be produced and maintained, and to its relatively low temperature coefficient. (See FALES and MUDGE, *J. Am. Chem. Soc.*, **42**, 2434 (1920).)

For the combination of an iodine electrode, whose ions are negatively charged, with a lead electrode we obtain the following expression:

$$E = 1.983 \cdot 10^{-4}\, T \left(-\, log\, \frac{a_{I^-}}{A_{0I^-}} - \frac{1}{2}\, log\, \frac{a_{Pb^{++}}}{A_{0Pb^{++}}} \right) \qquad (223)$$

When E written in this manner assumes a positive value, it signifies that the electrode in the first position will be positively charged. Now we may expediently substitute E_0 for the constant quantity $\pm \frac{1.983 \cdot 10^{-4}}{ne}\, T\, log\, \frac{1}{A_0}$, where the positive sign holds for positive ions and the negative for negative ions. Equations (222) and (223) then assume the following form.

$$E = \frac{1.983 \cdot 10^{-4}}{2}\, T\, log\, \frac{a_{Cu^{++}}}{a_{Zn^{++}}} + E_{0Cu} - E_{0Zn}, \qquad (222a)$$

$$E = 1.983 \cdot 10^{-4}\, T\, log\, \frac{1}{a_I \cdot a_{Pb^{++}}^{\frac{1}{2}}} + E_{0I} - E_{0Po}. \qquad (223a)$$

Therefore, in order to calculate the *e.m f.* of such a galvanic element, the difference $E_{0_1} - E_{0_2}$ must be known in addition to the ratio of the ionic activities. It is not important to establish the absolute values of E_0, which are difficult to estimate with certainty, but, instead, only their differences which we can arbitrarily establish for a definite normal electrode of the value $E_0 = 0$. According to a proposal of Nernst, this is done for a **normal hydrogen electrode,** *i.e.*, a platinum foil bathed with hydrogen under atmospheric pressure which dips in a solution normal in respect to hydrogen ion. This hydrogen electrode represents the zero point for the E_0 value. When we place the E_0 values in the order of their magnitude, we get the so-called potential series of the elements (Table 46), whose numbers are directly obtained experimentally according to Eq. (222*a*) as the potential difference between an electrode dipping in a normal ion solution and a normal hydrogen electrode. A potential series of the elements measured in volts against the normal hydrogen electrode in aqueous solution[1] are given in Table 46

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[1] It is conceivable that differences may very well exist between the potential series in a non-aqueous solution and those indicated in Table 46, though, as measurements concerning this show, they do not appear to be very considerable. See, among others, NEUSTADT, *Z. Elektrochem.*, **16**, 866 (1910).

The use of the numbers of Table 46 for the calculation of the *e.m.f.* of a galvanic element may be explained by the following example: let $a_{Cu^{++}} = a_{Zn^{++}}$. Then E reduces to

$$E_{0Cu} - E_{0Zn} = +0.34 - (-0.76) = 1.10 \text{ volts.}$$

Every tenfold decrease of Cu^{++} ion activity reduces E exactly $\frac{0.058}{2} = 0.029$ *volt;* every tenfold decrease of Zn^{++} ion activity raises E by an equal amount.[1]

TABLE 46.*—POTENTIAL SERIES OF ELEMENTS IN AQUEOUS SOLUTIONS MEASURED IN VOLTS AGAINST THE NORMAL HYDROGEN ELECTRODE

Li/Li^+	−2.9578	$H_2/2H^+$	±0.0000
Rb/Rb^+	−2.9242	Cu/Cu^{++}	+0.3448
K/K^+	−2.9224	Cu/Cu^+	+0.51
Na/Na^+	−2.7125	Ag/Ag^+	+0.7995
Mg/Mg^{++}	−1.55	Hg/Hg_2^{++}	+0.7986
Zn/Zn^{++}	−0.7581	Au/Au^+	+1.5
Fe/Fe^{++}	−0.44	Anion formation	
Cd/Cd^{++}	−0.40	S^{--}/S (solid)	−0.55
Tl/Tl^+	−0.336	$4OH^-/O_2 + H_2O$	+0.41
Ni/Ni^{++}	−0.22	$2I^-/I_2$ (solid)	+0.5357
Sn/Sn^{++}	−0.136	$2Br/Br_2$ (liquid)	+1.0659
Pb/Pb^{++}	−0.122	$2Cl^-/Cl_2$ (gas)	+1.3594
Fe/Fe^{+++}	−0.045	$2F^-/F_2$ (gas)	+1.9

* Numerical values revised by translators. The convention in sign is that of the original, which is opposite to that used by some writers in America.

Equation (222) and Table 46 are of importance in purely chemical respects, because with their help we may calculate whether and how far a (base) metal which is introduced into an aqueous ionic solution of another more noble metal may precipitate the latter as metal. A trace of the nobler metal is precipitated upon the less noble metal the moment it is introduced into the solution, and we then have a galvanic element, noble metal = solution = base metal, which is short-circuited within itself. The *e.m.f.* originally present is, therefore, quickly compensated, since the ionic concentration of the baser metal increases and that of the nobler metal decreases. Equilibrium is set up when $E = 0$ according to Eqs. (222*a*) and (223*a*).

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[1] The addition of sufficient quantity of KCN to the copper solution of a Daniell cell reduces the copper-ion content so much, owing to the formation of complex ions, that the cell reverses the sign of its potential.

215. The Equilibrium of Ions of Difference Valence.—This result may be applied to the question, What is the equilibrium between cupro and cupric ions in the presence of metallic copper? Imagine a strip of copper dipping in a solution containing some cupric ions and another in one containing cuprous ions and the two electrodes connected. The same result is obtained if a single strip of copper is introduced in a solution which contains cupric ions as well as cuprous ions. For equilibrium at room temperature we have

$$E = 0.058 \; log \; \frac{a_{Cu^+}}{a^{1/2}_{Cu^{++}}} + 0.51 - 0.34 = 0.$$

When $a_{Cu^{++}} = 1$, then $a_{Cu^+} \simeq 10^{-3}$; on the other hand, when $a_{Cu^{++}} = 10^{-10}$ $a_{Cu^+} = 10^{-8}$. The cupric ion is in excess for equilibrium in higher ionic concentrations while at lower concentrations, such as in potassium cyanide solutions, the cupro ion exists in excess

216. Amalgam Electrodes.—While the solution tension A_0 or E_0 has a definite value for pure compact metals, it may be markedly reduced if the electromotively active metal is dissolved in a more noble liquid metal (mercury). The solution tension of pure metallic sodium is so considerable that it liberates H_2 violently in the presence of water On the other hand, a dilute sodium amalgam solution is not decomposed appreciably by water, due in part to the considerable overvoltage of H_2 on mercury. It is clear that the solution tension of an amalgamated metal will be proportional to the activity a' of its dissolved monotomic metal atoms, since the higher the fugacity of the metal atoms in mercury the greater will be the tendency for them to go over into the ionic state in the solution from the mercury Therefore

$$A_0 = Const \; a'$$

When the metal whose concentration may be expressed by the activity a_n forms predominately m-atomic molecules in mercury then the following holds within the mercury according to the L M A

$$\frac{a'^m}{a_n} = K' \quad \text{or} \quad a' = \sqrt[m]{K' a_n} = \frac{A_0}{Const}$$

The *e m f* of a single amalgam electrode (of a univalent metal) at room temperature is, therefore,

$$E = 0.058 \; log \; \frac{a_i}{A_0} = 0.058 \; log \; \frac{a_i}{a' \, Const} = 0.058 \; log \; \frac{a_i}{\sqrt[m]{a_n}} - E_0'.$$

when we set the expression 0.058 log $Const \; \sqrt[m]{K'} = E_0'$ If we make a so-called amalgam cell by inserting two amalgam electrodes of different concentrations in the same solution, then the ion activity a_i and E_0' disappear and we obtain:

$$E = 0.058 \; log \; \frac{a_2'}{a_1'}, = \frac{0.058}{m} \cdot log \; \frac{a_{n_2}}{a_{n_1}}. \qquad (224)$$

A comparison of this formula with experimental data leads to the result that $m = 1$ for most metals *These metals are therefore dissolved in the monatomic state in mercury.*

217. Gas Electrodes.—For gas electrodes, which can be produced in many cases by bathing a sheet of metal (platinum) with a gas, the relations are similar to those for amalgam electrodes. The condition necessary for the appearance of a definite potential of a gas electrode is that the gas forms ions and that the ions appear in noticeable quantity in the charged state within or upon the electrode. These conditions are not fulfilled for a number of gases (N_2, CO, CO_2, CH_4), but they are approximately fulfilled for oxygen, and sufficiently so for hydrogen and the halogens that we may obtain electrodes of good reproducibility. If we now consider a hydrogen electrode, according to the L M A , we have within the metal for the equilibrium between hydrogen atoms H_m and hydrogen molecules H_{2m} (see **197**):

$$\frac{a^2_{H_m}}{a_{H_{2m}}} = Const. \quad \text{or} \quad a_{H_m} \sim \sqrt{p_{H_2}}$$

But from the distribution law $a_{H_{2m}}$ is proportional to the partial pressure of the gaseous hydrogen. Further, the solution tension A_0' is proportional to the concentration of gas atoms in the metal just as with amalgam electrodes. Therefore.

$$A_0 \sim a_{H_m} \sim \sqrt{a_{H_{2m}}} \sim \sqrt{p_{H_2}}$$

We, therefore, substitute in place of A_0 in Eq (219a):

$$A_0 = A_0' p^{1/2}_{H_2}$$

For a single hydrogen electrode the result is:

$$E_{H_2} = 1.983 \cdot 10^{-4}\, T \, log \frac{a_{H^+}}{A_0} = 1.983 \cdot 10^{-4}\, T \, log \frac{a_{H^+}}{p^{1/2}_{H_2}} \quad (225)$$

Then the expression $\frac{1.983 \cdot 10^{-4}}{n_e} T \; log \; A_0' = E_0'$ has a value of zero in the preceding case, since the potential of a normal hydrogen electrode ($a_{H^+} = 1$, $p_{H_2} = 1$ *atm*) has been established as the zero point of the potential series

When we employ two hydrogen electrodes operating under different pressures p_2 and p_1, but dipping in the same electrolyte, we obtain for the *e.m f.* of such a "**gas cell**" simply:

$$E_{H_2} = \frac{1.983 \cdot 10^{-14}}{2} T \, log \frac{p_2}{p_1}. \quad (226)$$

For an oxygen electrode in an OH^- ion solution we can put:

$$A_0 \sim a_{OH} \sim a^{1/4}_{O_2} \sim p^{1/4}_{O_2}$$

since the relation $a_{O_2} = k' \cdot (a_{OH\,\text{neutral}})^4$ must hold for the concentration of the hypothetical substance OH, which in any case is present in exceedingly small amounts according to the equation $O_2 + 2H_2O = 4OH$. In place of Eqs. (225) and (226) we obtain, on taking account of the negative charge of the OH ions,

$$E_{O_2} = 1.983 \cdot 10^{-4}\, log\, \frac{p^{1/4}_{O_2}}{a_{OH^-}} + E_0, \tag{225a}$$

where $E_0 = 0.41$ volt from Table 46; it follows for two oxygen electrodes in the same electrolyte that

$$E_{O_2} = \frac{1.983 \cdot 10^{-4}}{4}\, T\, log\, \frac{p_1}{p_2}. \tag{226a}$$

For a combination of two gas electrodes which form different ions, for example, a hydrogen-chlorine cell, we obtain in connection with Eq. (225) that:

$$E = 1.983 \cdot 10^{-4}T \left\{ -\, log\, \frac{a_{Cl^-}}{p^{1/2}_{Cl_2}} - log\, \frac{a_{H^+}}{p^{1/2}_{H_2}} \right\} + E_{HCl_2} - 0$$

and from a consideration of Table 46

$$E = 1.983 \cdot 10^{-4}T\{\tfrac{1}{2}\, log\, p_{Cl_2}p_{H_2} - log\, a_{Cl^-}a_{H^+}\} + 1.36. \tag{227}$$

An increase in the partial pressures of the gases, therefore, causes the *e.m.f.* of the cell to increase, while, on the contrary, an increase in the ionic concentrations decreases it.

The application of HCl as electrolyte in the *chlorine-hydrogen cell* yields a gas-cell of the type of Eq. (226), since the HCl existing as a gas over the solution is dissociated into H_2 and Cl_2 only to a minute degree. The electrode bathed by the chlorine is, therefore, similar to the hydrogen electrode and the partial pressure of the hydrogen amounts to

$$p_{H_2} = K\, \frac{p^2_{HCl}}{p_{Cl^2}}.$$

We may substitute the numerical value of $E = 1.3660$ *volt* in Eq. (226), which is that found for the H_2/Cl_2 cell in normal HCl at 298°C. and 0.987 *atm.*, and obtain $p_1 = p_{H_2} = 5.26\ 10^{-47}$ *atm.* as the partial pressure of hydrogen in the chlorine electrode. Since p_{HCl} can be estimated directly as 2.96×10^{-7} *atm.* and

p_{Cl_2} amounts to 0.987 *atm.*, we find $K = 6 \cdot 10^{-34}$ as the dissociation constant of gaseous HCl at room temperature.

We obtain Eq. (228) in a manner analogous to Eq. (227) by the union of Eqs. (225) and (225*a*) for the ordinary H_2/O_2 cell, whose O_2 electrode dips in a H^+ ion solution.

$$E = 1.983T\ (log\ p^{1/4}{}_{O_2} p^{1/2}{}_{H_2} - log\ a_{H^+} a_{OH^-}) + 0.41. \qquad (228)$$

Where both electrodes dip the same solution, the product $a_{H^+} a_{OH^-}$ has a value of about 10^{-14} at room temperature according to Table 34, and for the *e.m.f.* of the oxyhydrogen cell we find:

$$E = 1.23_4 + 1.983 \,.\, 10^{-4} T\ log\ p^{1/4}{}_{O_2} p^{1/2}{}_{H_2}. \qquad (228a)$$

The *e.m.f.* of the cell falls when the gas pressure decreases. Theoretically, the partial pressures of the O_2 and the H_2 may be decreased to that of the equilibrium concentration in water vapor, and in this limiting case no work can be extracted and E must drop to zero. The equilibrium partial pressures p_{O_2} and p_{H_2} of saturated water vapor at room temperature therefore may be obtained from the expression

$$1.23_4 + 0.058\ log\ p''_{H_2}{}^{1/2} p''_{O_2}{}^{1/4} = 0, \qquad (228b)$$

from which it follows that

$$p''_{H_2}{}^{1/2} p''_{O_2}{}^{1/4} = 0.6 \cdot 10^{-21} \qquad (229)$$

and for pure water vapor, where p''_{H_2} to p''_{O_2} are in the ratio of 2 to 1.

$$p''_{H_2} = 3.4 \cdot 10^{-29} atm.;\ p''_{O_2} = 1.7 \cdot 10^{-29} atm.$$

Since the partial pressure of water vapor which is equal to the vapor pressure amounts to 0.0191 *atm.* at $T = 290°$, the equilibrium constant K for the formation of water vapor amounts to

$$K = \frac{p''^{2}_{H_2} p''_{O_2}}{p''^{2}_{H_2O}} = 5.39 \cdot 10^{-83} = 10^{-82\ 27}. \qquad (229a)$$

218. Oxidation-reduction Potentials.—In the past reduction of a chemical substance has usually meant the taking up of hydrogen, and oxidation the taking up of oxygen.

However, all reduction reactions (or oxidation reactions) may be separated into two groups, of which the following reactions are typical:

1. Reduction of ethylene to ethane.
2. Reduction of $FeCl_3$ to $FeCl_2$.

The first case involves merely the taking up of a neutral hydrogen atom by a neutral molecule. However, the second case involves an ionic reaction, for, if we write the reduction of $FeCl_3$ to $FeCl_2$ analogous to the preceding case in the form

$$FeCl_3 + \tfrac{1}{2}H_2 = FeCl_2 + HCl, \tag{230}$$

then the characteristic reaction, namely, the loss of a positive charge on behalf of the metal, is brought out more clearly by the ionic equation

$$Fe^{+++} + \tfrac{1}{2}H_2 = Fe^{++} + H^{+}. \tag{230}$$

We understand by reduction in such cases not merely the taking up of hydrogen but the change of an atom or ion from a state of higher to one of lower positive valence and, accordingly, oxidation is the change to a higher positive valence.

In the case first mentioned the reducing action of hydrogen (elementary) is dependent only upon its partial pressure An equilibrium is set up for a given partial pressure of hydrogen, *i.e.*,

$$\frac{p_{C_2H_4} \cdot p_{H_2}}{p_{C_2H_6}} = K \quad \text{or} \quad p_{H_2} = \frac{K \cdot p_{C_2H_6}}{p_{C_2H_4}}$$

Therefore, for the case where equilibrium is actually set up[1] an ethylene-ethane mixture which bathes a strip of platinum dipping in an acid solution behaves as a hydrogen electrode and we have, according to Eq (225),

$$E = 1.983 \cdot 10^{-4} T \log \frac{a_{H^+} \cdot p^{1/2}_{C_2H_4}}{K^{1/2} p^{1/2}_{C_2H_6}} =$$

$$1.983 \quad 10^{-4}\, T \log \frac{a_{H^+} \quad p^{1/2}_{C_2H_4}}{p^{1/2}_{C_2H_6}} + E_0',$$

in which the constants appearing in the term E_0' have been combined.

The relations in the second type of oxidation-reduction reactions are somewhat different. The conversion of an ion into one of lower positive valence depends not alone upon the concentration of dissolved H_2 but also upon that of the hydrogen ion. For the reduction of $FeCl_3$ (Eq. (230)) the L M.A. yields

$$\frac{a_{Fe^{+++}} \quad a_{H_2}^{1/2}}{a_{Fe^{++}} \cdot a_{H^+}}, \tag{230a}$$

---

[1] In these cases it is very difficult to produce an equilibrium experimentally.

i.e., a definite ratio of the ferric to ferrous ions in solution is produced only if the concentration of the neutral H_2 as well as that of the hydrogen ions possesses a definite value.

In an aqueous solution which contains ferrous and ferric ions and, of course, also H^+ ions, a certain activity of neutral H_2 is set up in the solution phase and in the gas phase we have a certain fugacity p_{H_2} according to Henry's law.

A platinum electrode dipping in a ferrous-ferric ion solution will therefore always behave as a hydrogen electrode. We have for the potential of this electrode, when we keep in mind the proportionality of a_{H_2} with p_{H_2} as well as Eqs. (225) and (230*a*):

$$E = 1.983 \cdot 10^{-4} T \; log \frac{a_{Fe^{+++}}}{a_{Fe^{++}}} + E_0', \qquad (230b)$$

in which the constants are again assembled in E_0'. In this case the hydrogen-ion concentration is eliminated. Now, since Eq. (225) may be brought into the form

$$E = 1.983 \cdot 10^{-4} T \; log \frac{a_{H^+}}{a_H} + E_0'',$$

in which a_H represents the activity of the extremely small concentration of H atoms in the solution, it is recognized that the same relation holds for $Fe^{++} + 1\mathfrak{F} = Fe^{+++}$ as for the reaction $H + 1\mathfrak{F} = H^+$.[1]

A number of E_0' values for such oxidation-reduction electrodes are to be found in Table 47. From Table 46 we can determine in which direction the current will flow for a combination of two electrodes in which the ion activities are equal to unity in all cases, *i.e.*, which element or which ionic species, in the sense of the second group of oxidation-reduction reactions, will be oxidized and which will be reduced.

---

[1] A simple relation was discovered by Luther between the potential, metal/n_e-valent ion ($E_{1,2}$), metal/m_e-valent ion ($E_{1,3}$), and the potential, n-valent ion/m-valent ion ($E_{2,3}$), namely

$$n_e E_{1,2} + (m_e - n_e) E_{2,3} = m_e E_{1,3}.$$

This relation depends upon the consideration that the electrical work which is necessary to convert an atom into an m-valent ion must be independent of the path.

TABLE 47.—OXIDATION REDUCTION POTENTIALS

(*a*) Charged ions		(*b*) Other oxidations	
Cu^+/Cu^{++}	+0.18	$NO + 2H_2O/NO_3^- + 4H^+$	+0.95
Sn^{++}/Sn^{++++}	+0.2	$Cr^{+++} + 4H_2O/HCrO_4^- + 7H^+$	+1.3
$Fe(CN)_6^{----}/Fe(CN)_6^{---}$	+0.40	$Mn^{++} + 2H_2O/MnO_2 + 4H^+$	+1.35
Fe^{++}/Fe^{+++}	+0.75	$Pb^{++} + 2H_2O/PbO_2 + 4H^+$	+1.44
$Hg_2^{++}/2Hg^{++}$	+0.92	$Cl^- + 3H_2O/ClO_3^- + 6H^+$	+1.44
Tl^+/Tl^{+++}	+1.24	$Mn^{++} + 4H_2O/MnO_4^- + 8H^+$	+1.52
Co^{++}/Co^{+++}	+1.8	$MnO_2 + 2H_2O/MnO_4^- + 4H^+$	+1.63
Pb^{++}/Pb^{++++}	+1.8	$O_2 + H_2O/O_3 + 2H^+$	+1.9

If, for example, the ferrous-ferric electrode possesses the value $E_0 = 0.75$ *volt*, this means that a positive current will flow from such an electrode to a normal hydrogen electrode or that the ferric ions will give their charges to the ferrous ions, while at the hydrogen electrode elementary hydrogen will be converted into its ion. Therefore, hydrogen under atmospheric pressure reduces ferric ion. On the other hand, a current will flow from the silver electrode to the ferric-ferrous electrode when we insert a silver electrode in a normal solution against the ferrous-ferric electrode and the potential will be $0.80 - 0.75 = 0.05$ *volt*, *i.e.*, the ferrous ions will be oxidized to ferric ions by the silver ions.

The partial pressure p_{H_2} over a ferrous-ferric ion mixture which would be approached by the action of a neutral reduction reaction[1] may be calculated directly from E_0 by means of Eq. (226), in which we shall consider the ferrous ferric electrode to be opposed to a normal hydrogen electrode (*i.e.*, $p_2 = 1$ in Eq. (226)). When all the concentrations, including that of the hydrogen ion, are equal to 1, we obtain $0.029 \log \frac{1}{p_{H_2}} = 0.75$, or $p_{H_2} = 10^{-26}$ *atm* for the ferrous-ferric electrode. This partial pressure of H_2 is only a little greater than that of the dissociation pressure of hydrogen in water vapor (see Eq. (229)). Furthermore, the ferrous-ferric electrode may also be considered as an oxidation electrode on the basis of:

$$Fe^{++} + \tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O = Fe^{+++} + OH^-.$$

The application of Eq. (228*a*) with $p_{H_2} = 1$ or Eq. (229) with $p_{H_2} = 10^{-26}$ leads to the value $p_{O_2} = 10^{-33}$ *atm.*, which is somewhat smaller than that of the equilibrium pressure. Therefore, a normal acid ferrous-ferric solution represents a weak reducing agent for neutral reduction reactions.

The reducing potential of the mixture may be varied if we choose other values for the ionic concentrations If the hydrogen-ion concentration is kept at a value of 1 and the ratio made $\frac{a_{Fe^{+++}}}{a_{Fe^{++}}} \simeq 15$, we arrive at a partial pressure of H_2 as well as of O_2 which corresponds to the dissociation equilibrium of water vapor, *i.e.*, the ability of ferrous-ferric mixture to oxidize or to reduce is now the same as that of water vapor. If the hydrogen-ion concentration is increased the reducing action is increased (see Eq. (230*a*)). If the acidity is diminished, the oxidizing action increases. Therefore, a ferrous-ferric ion mixture in neutral or weakly alkaline solution represents a weak oxidizing agent for neutral reactions.

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[1] * In an acid-base equilibrium neutrality is represented by $p_{H^+} = p_{OH^-}$ or $c_{H^+} = c_{OH^+} = \sqrt{10^{-14}} = 10^{-7}$; and, correspondingly, neutrality in an oxidation-reduction equilibrium *in aqueous solution* would be represented by $p_{H_2} = 2p_{O_2}$ = about 10^{-29}, as given in Eqs. (229) and (229*a*).

A number of reactions combine both types of oxidation or reduction, *i.e.*, a change in charge occurs at the same time with the taking up of hydrogen or oxygen. Therefore, the concentrations of H^+ ions or OH^- ions do not completely disappear from the expression corresponding to Eq. (230*b*), for the potential of such electrodes, as it does for neutral oxidation-reduction reactions. The corresponding values E_0' for such cases are given under (*b*) in Table 47.

* The transition between the two types may be explained as follows: the fundamental reaction in an oxidation-reduction process is the taking up of electrons: *viz.*,

$$\textit{Oxidant} + n \ominus \rightleftharpoons \textit{reductant}^{n-} \ (\textit{potential base}), \qquad (230c)$$

by which the reductant becomes negatively charged and therefore tends to act as a base by attracting hydrogen ions (simple positive charges) so that we have the acid-base equilibrium.[1]

$$\textit{Base}^{n-} \ (\textit{reductant}) + n \oplus \rightleftharpoons \textit{acid} \ (\textit{reductant } H_n) \qquad (230d)$$

superimposed upon this.

* The question whether an oxidant will take up hydrogen on reduction, as in ethylene, or will remain ionized, as $Fe^{+++} + \ominus \rightarrow Fe^{++}$ or $I + \ominus \rightarrow I^-$, depends entirely upon the magnitude of the acidic dissociation constant of the reductant and the $[H^+]$ of the solution. Thus, the ion $C_2H_4^-$ is a powerful base (the residue of an extremely weak acid, ethane), while I^- is an extremely weak base (the residue of a strong acid, HI). The older concept of reduction, namely, the taking up of hydrogen atoms, thus becomes a summation of a *true reduction* Eq. (230c) and a neutralization Eq. (230*d*) and should be designated as a **hydrogenation** to distinguish it when the latter step is irreversible, as is the case with ethylene (Conant).

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[1] See footnote 3, p. 308.

* This point of view has recently been tested among members of the quinone series, where it is found that the primary reaction in alkaline solutions may be represented by

$$Q + 2\ominus \rightleftarrows Q^{=} \qquad (230e)$$

and in acid solutions by

$$Q + 2H^{+} + 2\ominus \rightleftarrows QH_2 \qquad (230f)$$

Here Q refers to a quinone and QH_2 to a hydroquinone. Now the hydroquinones behave as weak acids (in the case of benzohydroquinone $K_{a1} = 10^{-10}$ and $K_{a2} = 10^{-12}$) and in sufficiently alkaline solution they exist entirely in the form of the ion $Q^{=}$. The complete equation taking account of the stepwise ionization of the hydroquinone then becomes

$$E = E_0' + \frac{0.059}{2}\,log\,\frac{a_Q}{a_{QH_2}} - \frac{0.059}{2}\,log\left\{1 + \frac{K_{a1}}{a_{H^+}} + \frac{K_{a1}K_{a2}}{a^2_{H^+}}\right\} \qquad (230g)$$

For neutral and acid solutions where the reduced form exists almost entirely as undissociated QH_2, Eq (230g) may be simplified by collecting the acidic dissociation constants and E'_0 into one constant E_0, yielding

$$E = E_0 + \frac{0.059}{2}\,log\,\frac{a_Q}{a_{QH_2}} - 0.059\,log\,\frac{1}{a_{H^+}} \qquad (230h)$$

In the case of benzoquinone $E_0 = +0.6990$ at 25°C. Since a dilute equimolecular mixture of quinone and hydroquinone can be obtained by saturating the solution with their difficulty soluble addition product, quinhydrone, the term involving quinone and hydroquinone vanishes $\left(\log\frac{1}{1} = 0\right)$ and the hydrogen ion activity may then be calculated directly from the observed potential, by the equation

$$P_{H^+} = \log\frac{1}{a_{H^+}} = \frac{.6990 - E_{obs.}}{0.059} \qquad (230i)$$

Which follows from Eq. (230h). The *quinhydrone electrode* has certain advantages over the hydrogen electrode for the determination of acidity, in that it is capable of giving accurate results in the presence of unsaturated compounds like fumaric and maleic acids (Biilmann) and salts like $CuSO_4$ (LaMer) which poison the hydrogen electrode by their oxidizing properties. It reaches equilibrium rapidly and eliminates the necessity of using gaseous hydrogen, but unfortunately is unstable in solutions more alkaline[1] than $a_{H^+} = 10^{-7.5}$.

For example, consider the permanganate-manganous electrode, *i e*, a strip of platinum dipping in a permanganate-manganous ion solution. According to the reaction.

$$MnO_4^- + 3H^+ + {}^5\!/_2H_2 = Mn^{++} + 4H_2O$$

The following equilibrium is set up in solution

$$\frac{a_{Mn^{++}}}{a_{MnO_4^-} \cdot a^3_{H^+}} K = a^{5/2}_{H_2} \sim p^{5/2}_{H_2} \quad \text{or} \quad \frac{a_{H^+}}{p^{1/2}_{H_2}} = \frac{a^{1/5}_{MnO_4^-} \cdot a^{8/5}_{H^+}}{a_{Mn^{++}} \cdot K^{1/5}}.$$

From this we obtain

$$E = \frac{1.983 \cdot 10^{-5}}{5} T \log \frac{a_{MnO_4^-} \cdot a^8_{H^+}}{a_{Mn^{++}}} + 1.52 \qquad (231)$$

for the potential against a normal electrode. Making all concentrations equal to unity and substituting the value $E = 1.52$ remaining in Eq (228*a*) 10^{20} *atm.* is obtained for p_{O_2} when p_{H_2} equals unity, *i e*, this electrode exhibits a marked oxidizing action By a corresponding change in concentrations, such as on increasing the hydrogen-ion concentration, the effective partial pressure of the oxygen can be increased even further. That oxygen does not develop directly and escape as a gas in these simple conditions depends upon the phenomenon of "overvoltage," which will be discussed in detail later in Eq. (253)

c. The Relation between the Change of Heat Content and the Maximum Available Work

219. Calculation of the Heat Content of a Process from the Maximum Available Work.

—Equation (56), which depends upon the Second Law and which is valid for isothermal and isopiestic processes, forms the basis of the connection between the heat of reaction and the maximum work $A_{T,p}$. Here it assumes the form

$$A_{T,p} - H' = T\left(\frac{\partial A_{T,p}}{\partial T}\right)_p, \qquad (232)$$

if the heat of reaction H' is introduced in place of H.

From this we can calculate H' for every temperature so far as $A_{T,p}$ and, therefore, $\left(\frac{\partial A_{T,p}}{\partial T}\right)_p$ is known as a function of T.

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[1] * For a detailed discussion of oxidation potentials and acidity, see CLARK, WM M., and co-workers, *U S Pub Health Repts*, **38**, 666, 933, 1669 (1923), **39**, 381, 804 (1924); also CONANT, *et al*, *J. Am Chem Soc*, **44**, 1382 (1922). For a more detailed discussion of their application to the quinhydrone electrode see LAMER and PARSONS, *J. Biol. Chem*, **42**, 613 (1923), and LAMER and RIDEAL, *J. Am. Chem. Soc.*, **46**, 223 (1924).

If, therefore, the maximum work of a process can be measured directly as the *e.m.f.* of a galvanic element, we have from Eq. (216*a*) that

$$H' = 23050\, n_e\left[E - T\left(\frac{\partial E}{\partial T}\right)_p\right] \textit{cal.} \qquad (232a)$$

Equation (232*a*) has been the subject of frequent and careful experimental work (first by H. Jahn), and, in so far as the elements used were reversible, it has always been confirmed. Some of the Jahn's numerical results are reproduced in Table 48. While $T\left(\frac{\partial E}{\partial T}\right)_p$ exhibits only the character of a correction term in the first four cells, it is of so much importance in the calomel-mercuric oxide cell that the maximum available work = 23050 n_eE and the heat of reaction actually possess different signs.

TABLE 48.—THE HEATS OF REACTION OF SOME GALVANIC ELEMENTS

Element	*E* in *volts* at 0°C.	$\frac{\partial E}{\partial T}\left(\frac{volt}{deg.}\right)$	n_e 23050 $\left(E - T\frac{dE}{dt}\right)$ (*cal*)	H' obs (*cal*)
$Zn/ZnSO_4$ sat $Cu/CuSO_4$ sat	1.0934 (15°)	$-4.3\ 10^{-4}$	56090	55200
$Cu/Cu(C_2H_3O_2)_2aq$ $Pb/Pb(C_2H_3O_2)_2\ 100H_2O$	0.4764	$+3.85\ 10^{-4}$	17120	16520
$Ag/AgCl$. $Zn/ZnCl_2 \cdot 5H_2O$.	1.0171	$-2.1\ 10^{-4}$	49540	49080
$Ag/AgBr$ $Zn/ZnBr_2 \cdot 25H_2O$	0.84095	$-1.06\ 10^{-4}$	40100	39940
$Hg/Hg_2Cl_2 + KCl$. $Hg/Hg_2O + KOH$ . .	0.1483	$+8.37\ 10^{-4}$	−3710	−3280

220. Integration of the Fundamental Eq. (232).—While H' can be calculated directly by Eq. (232) when the absolute value of $A_{T,p}$ and its temperature coefficient are known, the reverse calculation of $A_{T,p}$ from H' and its temperature curve cannot be accomplished without further assumptions.

When H' is given as a function of temperature, the differential Eq. (232) merely states that at every point the value of H' increased by $T\left(\frac{\partial A_{T,p}}{\partial T}\right)_p$ is equal to $A_{T,p}$. But, as Fig 53 shows, an infinite number of $A_{T,p}$-curves correspond to one H'-curve.

This result is represented algebraically as follows: If the expression identical with Eq. (232) is integrated, the result is at

$$\frac{A_{T,p}\,dT - T\,dA_{T,p}}{T^2} = d\left(-\frac{A_{T,p}}{T}\right) = \frac{H'dT}{T^2}$$

constant pressure, so that the indefinite integral is first obtained:

$$\frac{-A_{T,p}}{T} = \int \frac{H'dT}{T^2} + Const\,, \tag{233}$$

which may be calculated except for an undetermined constant, when H' is known as a function of the temperature.

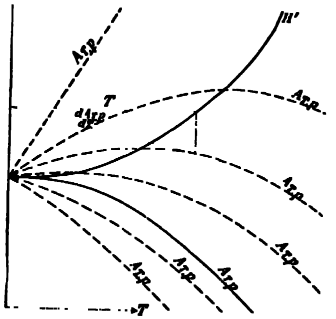

FIG. 53

Further, if $A_{T,p}$ is given for one temperature, this integration, and therefore the entire $A_{T,p}$-curve, becomes absolutely determined. For example, if we set $A_{T,p} = A_{T,p1}$ for $T = T_1$, we get:

$$-\frac{A_{T,p}}{T} + \frac{A_{T,p1}}{T_1} = \int_{T_1}^{T} \frac{H'}{T^2}dT$$

or

$$A_{T,p} = -T\int_{T_1}^{T} \frac{H'}{T^2}dT + \frac{A_{T,p1}T}{T_1}\,. \tag{233a}$$

221. The Connection between the Heat Content and the Equilibrium Constants of Gas Reactions.—An exceedingly important relation between the heat content and the equilibrium constant K_p for gas reactions is reached, if the value for $A_{T,p}$ given in Eq. (214a) is substituted in Eq. (232):

$$H' = A_{T,p} - T\left(\frac{\partial A_{T,p}}{\partial T}\right)_p = RT\,ln\,\frac{p_A{}^m p_B{}^n \cdots}{p^q{}_{A'}p^r{}_{B'}\cdots} - RT\,lnK_p$$

$$- RT\,ln\,\frac{p_A{}^m p_B{}^n \cdots}{p^q{}_{A'}p^p{}_{B'}\cdots} + RT\,lnK_p + RT^2\frac{dlnK_p}{dT}.$$

Since the expressions containing the initial and final partial pressures are to be handled as constants in differentiation, and therefore drop out, we have

$$H' = RT^2 \frac{d\,lnK_p}{dT} \qquad (234)[1]$$

Therefore, if K_p is known as a function of temperature, H' follows directly.

Equation (234) *states that a positive (exothermic) heat of reaction always corresponds to an increase of the constant* K_p *with an increase of temperature.* Since, every reaction may be considered as exothermic by writing it in that manner, K_p must always increase with increasing temperature in the examples given (numerical proofs are contained in Table 56 and elsewhere).

It should be noted that Eq. (234) may be looked upon as a generalization of the simplified Clapeyron-Clausius Eq (131*a*), for in vaporization or solution Eq (131*a*) is obtained directly from Eq. (234), when we set $K_p = p$ and $H' = \Lambda$.

Equation (234), first derived by van't Hoff, is frequently quoted as an expression of a general law, the **Le Chatelier-Braun principle,** which may be formulated as follows

> Every external influence (such as heating or compression) upon a mobile system produces a change in such a direction that the resistance of the system towards the external influence is increased as a result of this change

Now according to Eq. (234) the equilibrium of a chemical system is displaced by heating, so that a part of the heat of reaction H' is absorbed, as a result of the increase of K_p Hence, such a system uses more heat for a temperature increase, and therefore in such an act presents a greater resistance against it than does a system whose equilibrium is not displaced on heating.

The Le Chatelier-Braun principle may be considered in connection with the Second Law, but, since it leads only to a qualitative statement of this law, it yields much less than does the latter. Further, since it works correctly only when the variables of the state of the system are correctly chosen, as emphasized by the critical studies of Ehrenfest,[2] a direct application of the

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[1] The same equation holds for U', if K_c is substituted for K_p.

[2] *Z. physik. Chem*, **77**, 227 (1911).

Second Law is distinctly preferable to the Le Chatelier-Braun principle for obtaining this formula.

In order to use the differential Eq. (234) for calculations, it is expedient to integrate over a small temperature interval (between T_1 and T_2) within which H' may be regarded as constant. The result is then:

$$\ln K_{p1} - \ln K_{p2} = \frac{H'}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \frac{H'}{R}\frac{(T_1 - T_2)}{T_1T_2},$$

and if decadic logarithms and the value of R in heat units are introduced, this equation becomes:

$$\log K_{p1} - \log K_{p2} = \frac{H'}{4.571}\frac{(T_1 - T_2)}{T_1T_2} \qquad (234a)$$

The formation of NH_3 may be discussed again as an example of the application of this equation. Experimentally, K_p amounts to $6.3 \cdot 10^5$, for $T = 893°$ and $2.16 \cdot 10^6$ for $973°$,[1]

$$H' = \frac{4.571 \cdot 893 \cdot 973\ (\log 2.16 \cdot 10^6 - \log 6.3 \cdot 10^5)}{973 - 893} = 26550\ cal,$$

while direct calorimetric measurement at 932° yields 26,300 *cal.*

In order to integrate Eq. (234) over any range of temperature, H' is represented as a function of temperature by means of Kirchhoff's law (Eq. (212)) and then

$$\frac{d\ln K_p}{dT} = \frac{H_0' + \int_0^T \Sigma C'_p dT}{RT^2} = \frac{H_0' + \Sigma C'_{p0}T + \int_0^T \Sigma C'_T dT}{RT^2}, \qquad (234b)$$

where the molecular heats are split up into a portion independent of temperature C'_{p0} and a portion changing with temperature C'_T. We obtain, then, analogous to Eq. (131*b*) by integrating with $R = 1.986$ and introducing decadic logarithms:

$$\log K_p = -\frac{H_0'}{4.571T} + \frac{\Sigma C'_{p0}}{1.986}\log T + \frac{1}{4.571}\int_0^T \frac{dT}{T^2}\int_0^T \Sigma C_T' dT + J. \qquad (234c)^2$$

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[1] Haber, *Z. Elektrochem.*, **20,** 598 (1914).

[2] The assumption involved in this form of the equation is that C_T' rises more rapidly than in proportion to T to the first power in the immediate neighborhood of the absolute zero, since the integral $\frac{1}{R}\int_0^T \frac{dT}{T^2}\int_0^T \Sigma C_T' dT$ would be infinite for the lower limit. As far as previous experience extends, this condition is always fulfilled.

An integration constant also enters here which, in contrast to Eq. (233), must possess a definite numerical value, but its determination lies outside of the domain of classical thermodynamics.

222. The Nernst Heat Theorem.—The task of choosing the correct curve from the multiplicity of $A_{T,p}$-curves corresponding to an H'-curve, without previous knowledge of a point on the same, may be solved by the help of a new principle—**the Nernst Heat Theorem.**

The latter, like the two classical laws, is founded upon experience. It depends upon the fact, discussed previously, that solid bodies, in general, approximate to an ideal limiting state in which their properties become independent of the temperature. Therefore, the maximum work $A_{T,p}$ must also become constant in the immediate neighborhood of the absolute zero, or the differential quotient $\left(\frac{\partial A_{T,p}}{\partial T}\right)_p$ must equal zero, just as the differential quotient $\left(\frac{\partial H'}{\partial T}\right)_p$ disappears there according to Eqs. (211*a*), (60), and (88). Now, since $H' = A_{T,p}$ at absolute zero on the basis of Eq. (232), it follows as the essence of the Nernst Heat Theorem that the H'- and $A_{T,p}$-curves converge and fuse into one another just above the absolute zero, and proceed parallel to the T-axis.

It is clear that this result holds only for such substances which assume the properties of ideal solid bodies in the neighborhood of the absolute zero, and therefore the Nernst Heat Theorem refers in its simplest wording to "condensed systems," i.e., systems in which exchange occurs only between solid and liquid substances.[1]

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[1] A complete presentation of the basis and application of the Nernst Heat Theorem may be found in POLLITZER, F., "Berechnung Chemischer Affinitaten nach dem Nernstchen Warmetheorem," Stuttgart (1912), Enke, NERNST, W., "Theoretische und Experimentelle Grundlagen des neuen Warmesatzes," 2nd ed , Halle (1922), further, EUCKEN, A., *Ergebn. d exakt. Naturwissensch.*, p. 120 *et seq* , Berlin (1922).

[*] Since 1917 a number of valuable papers have appeared in English by G N. Lewis and his associates Gibson, Latimer, Rodebush, Eastman, and others, which fully confirm this phase of Nernst's principle. The reader interested in this important phase of thermodynamics will do well to read Chap. XXXI *et seq.* of Lewis and Randall's "Thermodynamics," as well as the articles referred to above, as he will gain a further insight into the causes

The cases in which a complete disappearance of $\left(\frac{\partial A_{T,p}}{\partial T}\right)_p$ can be established by measurements at accessible temperatures are not numerous, yet there are a great number of examples where it always becomes smaller with decrease of temperature, so that an extrapolation to the limiting state is scarcely burdened with any assumptions of an arbitrary character. Of the examples belonging to this class we will discuss at this point only the transition of white into gray tin, mentioned above, which was exhaustively studied by Brønsted (*Z. physik. Chem.*, **88**, 479 (1914)). The atomic heats of both modifications were measured between $T = 80°$ and $T = 300°$, from which the temperature curve of H' was established by means of Kirchhoff's law. The difference of the atomic heats could be represented by the formula (valid only for the temperature interval given above)

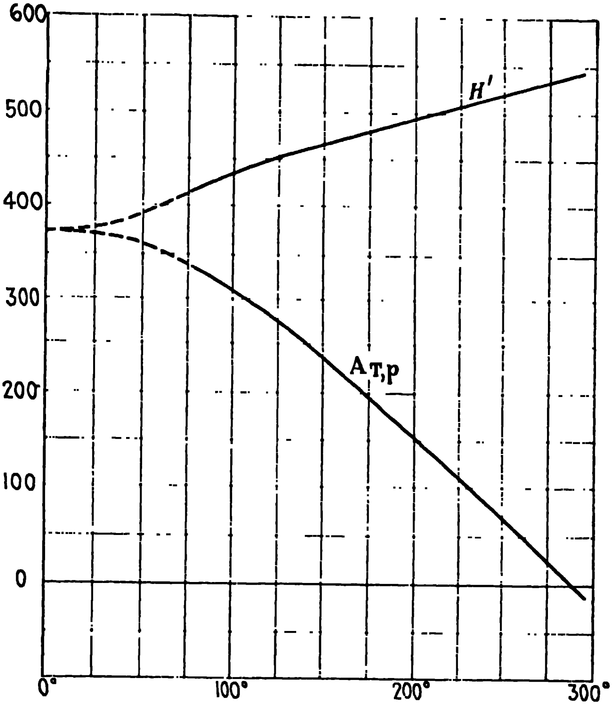

FIG. 51

$$C_w - C_g = 0.49 + 3.25 \cdot 10^{-8}(300 - T)^3$$

(C_w refers to the white, and C_g to the gray modification). Since H' amounts to 532 *cal.* at $T = 273°$, it follows that

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of the limitations of the principle to solutions and mixed crystals. See also p. 190 and EASTMAN, *J. Am. Chem. Soc.*, **46**, 39 (1924).

$$H_T' - H_{273}' = \int_{273}^{T}(C'_w - C'_g)dT = \int_{273}^{T}0.49dT + \int_{273}^{T}3.25\ \ 10^{-8}\,(300 - T)^3 dT$$

or

$$H' = 331.4 + 1.365T - 4.37\ \ 10^{-3}T^2 + 9\ 75\ \ 10^{-6}T^3 - 8\ 1\ \ 10^{-9}T^4.$$

Now, $A_{T,p} = 0$ for the transition point $T = 292$. Therefore, substituting this value for $A_{T\ p1}$ as well as 292 for T_1, it follows that

$$A_{T,p} = T\int_{T}^{292}\frac{H'}{T^2}dT$$

$$= T\left[-\frac{331\ 4}{T} + 1\ 365 lnT - 4\ 37\ \ 10^{-3}T + 4.87\ \ 10^{-6}T^2 - 2\ 7\ \ 10^{-9}T^3\right]_T^{292}$$

$$= 331\ 4 - 3.143T\,log_{10}T + 5\ 677T + 4.37\cdot10^{-3}T^2 - 4.87\ \ 10^{-6}T^3 + 2\ 7\ \ 10^{-9}T^4.$$

From this it is clear, as shown in Fig 54, that the course of the curve (depending only upon the Second Law) joins the H'-curve

It shows that the H'- and the $A_{T,p}$-curve in fact always approach one another at low temperatures, and it appears highly probable that they fuse with each other at not only $T = 0$, but even somewhat above this temperature, as shown by the dotted lines. This equality of the maximum work $A_{T,p}$ with the change of heat content H', not only at the absolute zero itself but for a definite temperature range above the same, represents, as already stated above, the characteristic requirement of the Nernst Heat Theorem.

It is necessary to know the H'-curve in the immediate neighborhood of the absolute zero to test whether the fundamental requirement of the Nernst Heat Theorem is in harmony with the observations in all cases. However, only one point at higher temperatures on the $A_{T,p}$-curve need be known, as in the example of the transition point of the tin modifications. Now, instead of constructing the $A_{T,p}$-curve at lower temperatures by means of the Second Law, in so far as the H'-curve permits, as was done above, it is easier to choose a definite curve from the multiplicity of $A_{T,p}$-curves by the condition of its fusion with the H'-curve in the neighborhood of the absolute zero and then see whether the $A_{T,p}$ values actually observed at higher temperature lie upon this curve.

In order to obtain the correct $A_{T,p}$-curve analytically or, what amounts to the same thing, to fix the undetermined integration constant of Eq (233), we have the characteristic condition

$$\lim_{T=0}\frac{dH'}{dT} = \lim_{T=0}\frac{dA_{T,p}}{dT} = 0 \qquad (235)$$

to unite with Eq. (233).

On the basis of Kirchhoff's law we first obtain the definite integral in place of Eq. (233) for condensed systems,

$$A_{T,p} = H_0' - T\int_0^T \frac{dT}{T^2}\int_0^T \Sigma C_p dT + J_k T, \qquad (233b)$$

in which the integration constant J_k possesses for the present a fixed numerical value. The assumption is made in agreement with the experimental data previously given for the molecular heat of solid and liquid substances at very low temperatures that the molecular heat C_p rises at least proportional to T, since otherwise the integral expression contained in Eq. (233b) would be infinitely great for $T = 0$ similar to the above.

We obtain from Eq. (233b) by differentiation

$$\frac{dA_{T,p}}{dT} = -\int_0^T \frac{dT}{T^2}\int_0^T \Sigma C_p dT - \frac{1}{T}\int_0^T \Sigma C_p dT + J_k. \qquad (236)$$

Since the two integral expressions must vanish in the neighborhood of the absolute zero, owing to the assumed and experimentally established temperature curve of the molecular heat, it follows first that

$$\lim_{T=0} \frac{dA_{T,p}}{dT} = J_k.$$

Then in order that the condition of Eq. (235) be fulfilled the following must hold:

$$J_k = 0. \qquad (237)$$

Therefore, if the H'-curve of a condensed system is regarded as given empirically (in which the condition $\lim_{T=0} \frac{dH'}{dT} = 0$ must be fulfilled), then the *requirement that the integration constant vanishes suffices for establishing the correct $A_{T,p}$-curve.*[1] Hence we have for the maximum work of a process in a condensed system the expression

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[1] Just as the sum of the specific heats of the reacting substances may be added together according to Kirchhoff's law, we can think of J_k as being resolved in an analogous way into a sum in which each member represents a characteristic constant for the participants in the reaction. ($J_k = i_1 + i_2 + i_3 +$ $-i_1' - i_2'$.) While the original Nernst Theorem demanded only that J_k vanished for every reaction in a condensed system, Planck expressed the conjecture that the values i_1, i_2, i_3 i_1' . would be equal to zero for the individual solid bodies.

$$A_{T,p} = H_0' - T\int_0^T \frac{dT}{T^2}\int_0^T \Sigma C_p dT. \qquad (233c)$$

According to this the calculation of $A_{T,p}$ for a given temperature T requires a knowledge of:

1. The molecular heats of the reacting substances and their temperature curve from the temperature T down to the neighborhood of absolute zero.

2. The heat content of the reaction for a temperature between absolute zero and T, from which H_0' may be calculated by means of Eq. (212).

In numerous cases an exact test of Eq. (233c) can be carried out, *i.e.*, a comparison of the calculated $A_{T,p}$ values with those found experimentally. The result is that in all cases up to this time the agreement between the calculated and the observed values of $A_{T,p}$ is the more complete the more accurately the data (H', C_p, $A_{T,p}$) can be determined. Larger discrepancies which were evident in certain cases from the very first can without exception be traced back to errors of experiment or calculation. The exact empirical proof of Nernst's Heat Theorem indicated above can thus be considered as proved. This result signifies a confirmation of the fundamental theorem that all properties of solid bodies are independent of the temperature at very low temperatures

TABLE 49

$\Phi = \frac{1}{T}\int_0^T C_v dT$ for the Debye function $C_v = D\left(\frac{\Theta}{T}\right)$ (See 78)

$\frac{\Theta}{T}$	0 0	0 1	0 2	0 3	0 4	0 5	0 6	0 7	0 8	0 9	1 0
0	5 955	5 7330	5 5195	5 3122	5 1100	4 9130	4 7220	4 5364	4 3578	4 1862	4 0168
1	4 0168	3 8535	3 6951	3 5430	3 3991	3 2592	3 1229	2 9920	2 8640	2 7305	2 6266
2	2 6266	2 5138	2 4068	2 3047	2 2044	2 1078	2 0166	1 9288	1 8446	1 7642	1 6873
3	1 6873	1 6131	1 5123	1 4756	1 4118	1 3192	1 2917	1 2364	1 1825	1 1314	1 0821
4	1 0821	1 0361	0 9931	0 9517	0 9118	0 8733	0 8361	0 8002	0 7654	0 7317	0 7009
5	0 7009	0 6712	0 6438	0 6187	0 5944	0 5708	0 5478	0 5255	0 5037	0 4824	0 4618
6	0 4618	0 4437	0 4259	0 4088	0 3926	0 3787	0 3652	0 3519	0 3387	0 3257	0 3128
7	0 3128	0 3017	0 2908	0 2803	0 2702	0 2605	0 2513	0 2423	0 2340	0 2263	0 2195
8	0 2195	0 2135	0 2077	0 2017	0 1959	0 1905	0 1855	0 1797	0 1744	0 1691	0 1639
9	0 1639	0 1588	0 1536	0 1485	0 1435	0 1384	0 1336	0 1289	0 1242	0 1195	0 1149
10	0 1149	0 1107	0 1070	0 1038	0 1009	0 0983	0 0957	0 0931	0 0907	0 0886	0 0866

TABLE 50

$\Phi = \frac{1}{T}\int_0^T C''_T dT$ for the Planck-Einstein function $C''_T = \varphi\left(\frac{\Theta}{T}\right)$ *Equation* (98a)

$\frac{\Theta}{T}$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0	1.985	1.887	1.793	1.702	1.614	1.530	1.448	1.370	1.296	1.227	1.155
1	1.155	1.089	1.027	0.967	0.909	0.855	0.803	0.754	0.707	0.663	0.621
2	0.621	0.582	0.544	0.509	0.476	0.444	0.414	0.386	0.360	0.335	0.312
3	0.312	0.290	0.270	0.251	0.233	0.216	0.201	0.186	0.173	0.160	0.148
4	0.148	0.137	0.127	0.117	0.109	0.100	0.093	0.086	0.079	0.073	0.067
5	0.067	0.062	0.057	0.053	0.049	0.044	0.041	0.038	0.035	0.033	0.0300
6	0.030	0.0272	0.0250	0.0230	0.0211	0.0195	0.0179	0.0164	0.0150	0.0138	0.0127
7	0.0127	0.0116	0.0106	0.0098	0.0089	0.0083	0.0076	0.0069	0.0063	0.0058	0.0053
8	0.0053	0.0048	0.0045	0.0041	0.0038	0.0034	0.0031	0.0029	0.0026	0.0024	0.0022
9	0.0022	0.0020	0.0018	0.0017	0.0015	0.0014	0.0013	0.0012	0.0011	0.0010	0.0009
10	0.0009	0.0008	0.0008	0.0007	0.0006	0.0006	0.0005	0.0005	0.0004	0.0004	0.0004

TABLE 51

$\Psi = \int_0^T \frac{dT}{T^2}\int_0^T C_V dT$ for the Debye function $C_V = D\left(\frac{\Theta}{T}\right)$

$\frac{\Theta}{T}$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0		15.9180	12.0098	9.8111	8.3113	7.1921	6.3134	5.5993	5.0065	4.5030	4.0766
1	4.0766	3.6940	3.3650	3.0756	2.8192	2.5899	2.3839	2.1986	2.0307	1.8781	1.7414
2	1.7414	1.6158	1.5016	1.3973	1.3011	1.2125	1.1318	1.0573	0.9886	0.9851	0.8665
3	0.8665	0.8122	0.7619	0.7157	0.6731	0.6324	0.5954	0.5612	0.5290	0.4992	0.4708
4	0.4708	0.4449	0.4210	0.3985	0.3774	0.3576	0.3389	0.3212	0.3044	0.2885	0.2739
5	0.2739	0.2605	0.2476	0.2361	0.2251	0.2146	0.2047	0.1951	0.1860	0.1771	0.1688
6	0.1688	0.1613	0.1540	0.1474	0.1408	0.1351	0.1298	0.1246	0.1196	0.1146	0.1097
7	0.1097	0.1055	0.1014	0.0974	0.0937	0.0901	0.0868	0.0835	0.0801	0.0776	0.0751
8	0.0751	0.0730	0.0709	0.0687	0.0667	0.0646	0.0629	0.0609	0.0590	0.0572	0.0554
9	0.0554	0.0536	0.0518	0.0500	0.0483	0.0466	0.0449	0.0433	0.0417	0.0401	0.0386
10	0.0386	0.0371	0.0358	0.0348	0.0338	0.0329	0.0320	0.0311	0.0303	0.0296	0.0289

TABLE 52

$\Psi = \int_0^T \frac{dT}{T^2}\int_0^T C''_T dT$ for the Planck-Einstein function $C''_T = \varphi\left(\frac{\Theta}{T}\right)$

$\frac{\Theta}{T}$	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
0	∞	4.662	3.390	2.680	2.203	1.853	1.580	1.360	1.182	1.035	0.910
1	0.910	0.803	0.711	0.631	0.562	0.501	0.447	0.400	0.358	0.321	0.288
2	0.288	0.258	0.233	0.209	0.188	0.169	0.153	0.137	0.124	0.112	0.101
3	0.101	0.091	0.082	0.074	0.066	0.060	0.055	0.049	0.044	0.039	0.036
4	0.036	0.032	0.029	0.026	0.023	0.021	0.019	0.017	0.016	0.014	0.013
5	0.013	0.011	0.010	0.009	0.008	0.007	0.007	0.006	0.005	0.005	0.004
6	0.004	0.004	0.003	0.003	0.002	0.002	0.002	0.001	0.001	0.001	0.001
7	0.001										

223. Practical Application of the Nernst Heat Theorem to Condensed Systems.—Now, certain difficulties of calculation interfere with the practical application of Eq. (233c) because the double integrations to be undertaken in Eq. (233c) frequently lead to complicated formulas, the use of which, to say the least, is laborious and time-consuming. It is to be recommended, therefore, that the expression $\int_0^T \frac{dT}{T^2}\int_0^T \sum C'_p dT$ and the expression $\int_0^T \sum C'_p dT$ necessary for the determination of H_0' be first split up into its individual terms corresponding to the different reacting substances

$$\text{(I)} \quad \Psi_1 = \int_0^T \frac{dT}{T^2}\int_0^T C'_{p1}dT, \quad \Psi_2 = \int_0^T \frac{dT}{T^2}\int_0^T C'_{p2}dT$$

$$\text{(II)} \quad T\Phi_1 = \int_0^T C'_{p1}dT, \qquad T\Phi_2 = \int_0^T C'_{p2}dT \quad . \; .$$

and these values estimated in the form of tables.

If it may be assumed that the temperature curve of C'_v is represented with sufficient accuracy by Debye's function (see **78**), which may be abbreviated in what follows as $D\left(\frac{\Theta}{T}\right)$, the expression Φ is obtained simply by means of Table 49, and the expression Ψ by means of Table 51, in which in the argument $\frac{\Theta}{T}$ we must put the value of Θ determined from the temperature curve of the molecular heat, and for T we must put that temperature for which the calculations are to be performed. However, since the Debye function holds for C'_v while C'_p is to be applied here, the difference $C'_p - C'_v$ must be carried along as a correction term, which frequently has much weight at higher temperatures (see **64**). The Debye function does not render the temperature curve of C'_v with sufficient accuracy with only one Θ value for substances of complex molecular constitution, though in such cases it frequently permits a satisfactory representation with several values (see **61**).

As an example of the evaluation of Eq. (233c) by means of the tables, the maximum work may be calculated for the reaction already mentioned, $Pb + 2AgCl = PbCl_2 + 2Ag$, which may be ascertained at the same time experimentally as the *e m f* of the lead chloride-silver chloride cell The heat of the reaction measured calorimetrically amounts to 24,820 *cal* at 290° *abs.* The molecular heats C_p are represented with some approximation through the following expression, in which $C'_p - C'_v \sim T^{3/2}$.

$$\text{Pb} \quad D\left(\frac{88}{T}\right) + 7 \quad 10^{-5}T^{3/2}$$

$$2\text{AgCl} \quad 2\left\{ D\left(\frac{110}{T}\right) + D\left(\frac{250}{T}\right) + 22 \quad 10^{-5}T^{3/2}\right\}$$

$$\text{PbCl}_2 \quad D\left(\frac{85}{T}\right) + 2D\left(\frac{270}{T}\right) + 18 \quad 10^{-5}T^{3/2}$$

$$2\text{Ag} \quad 2\left\{ D\left(\frac{222}{T}\right) + 5 \quad 10^{-5}T^{3/2}\right\}$$

Therefore, it follows that

$$\frac{dH'}{dT} = \Sigma C_p = D\left(\frac{88}{T}\right) + 2D\left(\frac{110}{T}\right) + 2D\left(\frac{250}{T}\right) - D\left(\frac{85}{T}\right) - 2D\left(\frac{270}{T}\right)$$
$$- 2D\left(\frac{220}{T}\right) + 23 \quad 10^{-5}\,T^{3/2},$$

and from this, according to Table 49, for $T = 290°$ the result is

$$T\Sigma\Phi = \int_0^{290} \Sigma C'_p dT = 1536 + 2 \times 1492 + 2 \times 1232 - 1515 - 2 \times 1200$$
$$- 2 \times 1283 + \tfrac{2}{5} \times 23 \times 10^{-5} \times 290^{5/2} = 601.$$

This amounts to $H_0' = 24820 - 601 = 24219$ *cal*

Further, for $T = 290°$ according to Table 51

$$\Sigma\Psi = \int_0^T \frac{dT}{T^2}\int_0^T \Sigma C'_p dT = 9\ 76 + 2 \times 8\ 59 + 2 \times 4\ 70 - 9\ 92 -$$
$$2 \times 4\ 36 - 2 \times 5\ 20 + 9\ 2 \times 10^{-5} \times \tfrac{2}{3} \times T^{3/2} = 7.60.$$

and, therefore, for Eq (233*c*)

$$A_{T,p} = 24219 - 290 \times 7\ 60 = 22010.$$

Now H. Miething[1] has determined the expressions Φ and Ψ numerically for a great number of substances whose molecular heats are known down to low temperatures and has assembled them in comprehensive tables. These data were obtained by means of a graphic procedure. The C_p-curve found empirically was first plotted upon coordinate paper. The integral of the function $T\Phi = \int_0^T C'_p dT$ was obtained by measuring the surface area of the figure (see **10**). The function $\frac{1}{T^2}\int_0^T C'_p dT = \frac{\Phi}{T}$ was first represented in a similar way as a curve and then integrated graphically. Now the use of Miething's tables is very much simpler than that of the Debye function.

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[1] *Abhandl. Deut. Bunsengesell.*, Nr. 9.

We obtain directly for the case of the lead chloride-silver chloride cells for $T = 290°$

$$T\Sigma\Phi_{290} = 1593 + 4 \times 1396 - 3 \times 1356 - 2 \times 1316 = 477.$$

Therefore, $H_0' = 24343$ *cal.* Further

$$\Sigma\Psi_{290} = 9.91 + 4 \times 6.67 - 3 \times 6.49 - 2 \times 5.33 = 6.43$$

$$A_{T,p} = 24343 - 290 \times 6.43 = 22483 \text{ cal.}$$

Experimental measurements give 0.4889 *volt* for the *e.m.f.* of the lead chloride-silver chloride cell which corresponds to a free energy of 2 × 23050 × 0.4889 = 22540 *cal.* The agreement of this number with the value calculated from Miething's tables is excellent, while an error of some hundred calories is given by using the Debye function. The result that Miething's method points to a definite superiority is not surprising, since the Debye function does not always adapt itself completely enough to the course of the molecular heat of polyatomic substances even when several Θ values are used, while the graphic process always operates with the same accuracy even though it is only moderate. Also, the correction term for $C_p - C_v$ produces some inconvenience in the formal representation, while in the graphic process it is automatically taken care of.

In general, therefore, it is recommended that the maximum work of a reaction, for which the Debye function with a single Θ value does not suffice for the representation of the molecular heat of all reacting participants, be calculated, where possible, according to the graphic process if the necessary data are not contained in Miething's tables.

In conclusion, the following point deserves consideration in the determination of the maximum work of a condensed system. The function $\frac{\Phi}{T}$ passes through a maximum, since it increases faster at low temperatures and slower at high temperatures than does T. As a rule, this point lies below room temperature. Therefore, special care must be exercised in the evaluation of the integral $\Psi = \int \frac{\Phi}{T} dT$ in this temperature range and it is to be especially noted that *this also comes into marked prominence in the calculation of the maximum work at higher temperatures.*

224. Complete Thermodynamic Calculation of the Equilibrium of Gaseous Systems.—The transition from condensed systems to gaseous systems involves no theoretical difficulties. The system is first considered at such a low temperature that all reacting participants are present not only as gases but also as solid or liquid bodies. When it is considered that the reaction proceeds directly between the solid bodies, the maximum available work $A_{T,p\,(solid)}$ of the reaction is represented by Eq. (233*c*).

The operation may also be performed in a roundabout way through the gas phase. Since in the vaporization of the initial substances and in the condensation of the final products no work is performed, the expression (Eq. (214*a*)) holds for the total reaction

$$A_{T,p\,(gas)} = RT\left\{ln\frac{p_A{}^m p_B{}^n \cdots}{p^q{}_{A'}p^p{}_{B'}\cdots} - lnK_p\right\},$$

in which the pressures p_A and p_B, etc. represent the vapor pressures of the reacting substances in the preceding case.

On the basis of the Second Law the conclusion is, as usual, that $A_{(gas)} = A_{(solid)}$ and that, therefore,

$$RTln\frac{p_A{}^m p_B{}^n \cdots}{p_{A'}{}^q \cdots} - RTlnK_p = H_0' - T\int_0^T\frac{dT}{T^2}\int_0^T \Sigma C'_{p\,(solid)}\,dT.$$

We can eliminate the vapor pressure of the solid body directly by use of the general vapor-pressure Eq. (131*f*) and, by introducing decadic logarithms at the same time, obtaining:

$$log\ K_p = -\frac{H_0' + n\Lambda_{0A} + m\Lambda_{0B}\ \cdots\ - q\Lambda_{0A'}\ \cdots}{4.571T} +$$
$$\frac{1}{4.571}\int_0^T\frac{dT}{T^2}\int_0^T \Sigma C_T'dT + \frac{1}{1.985}\Sigma C_{p0}\,log\ T + ni_A +$$
$$mi_B\ \cdots - qi_A'\ \cdots,$$

in which C_T' and C_{p0} refer only to the gaseous substances, since the terms with $C_{p\,(solid)}$ etc. have disappeared. Now the expression $H_0' + n\Lambda_{0A} + m\Lambda_{0B}$ . . $q\Lambda_{0A'}$ . . . , *i.e.*, the heat content of the reaction of the solid substances increased by the sum of the heats of vaporization of the reacting substances and diminished by the sum of the heats of vaporization of the resulting products, is to be set equal to the heat content of the reaction in the gaseous phase H'_{0g} according to the First Law and, therefore, it is simply found that:

$$log\ K_p = -\frac{H'_{0g}}{4.571T} + \frac{1}{1.985}\Sigma C_{p0}\,log\ T +$$
$$\frac{1}{4.571}\int_0^T\frac{dT}{T^2}\int_0^T \Sigma C_T'dT + ni_A + mi_B\ \cdots - qi_{A'}\ \cdots,\ \ (234d)$$

an equation which is identical with Eq. (234c) if the previously unknown integration constant J is set equal to:

$$J = ni_A + mi_B \;.\quad .\; -qi_{A'} \;.\qquad , \qquad (238)$$

i.e., the *integration constant J of the differential Eq.* (234) *in gas reactions is equal to the sum of the chemical constants of the gas molecules disappearing diminished by the chemical constants of those which are formed (taking account of the number of moles involved).*

The course of K_p is established, as a rule, by the estimation of the integration constant J at a low temperature *Equation* (234*d*) *is, therefore, independent of the presence of solid bodies and also holds for any given high temperature*

225. The Independence of the Chemical Constants upon the Nature of the Solid Phase.—As the preceding considerations show, the specific nature of the solid body with which the gas equilibrium at low temperature is established requires no further discussion. Theoretically, it is quite the same, whether we work at a somewhat higher temperature where the substance is liquid, or at a lower temperature where it is solid. The final result is that Eq (234*d*) must be independent of these considerations, *i e.*, the constant, $J \;\; = ni_A + mi_B \qquad -qi_A' \qquad ,$ must possess a definite value, uninfluenced by the nature of the solid bodies chosen. Obviously, this is only possible if the term i possesses the same value for all condensed phases. The importance of this result may be confirmed in the following way Consider two condensed phases, such as liquid and crystal, which will, in general, possess different vapor pressures p and p' except at their transition (melting) point. The maximum work of transition is, therefore, represented by Eq. (213). We then obtain, at the same time keeping Eq. (131*f*) in mind, that:

$$A_{T,p} = RT\,lnp - RT\,lnp' = \Lambda_0 + C_{p0}T\,lnT +$$
$$T\int_0^T \frac{dT}{T^2}\int_0^T (C_T' - C_{p\,(solid)})\,dT + i + \Lambda_0' -$$
$$C_{p0}T\,lnT - T\int_0^T \frac{dT}{T^2}\int_0^T (C_T' - C''_{p\,(solid)})dT - i'$$

or

$$A_{T,p} = \rho_0 - T\int_0^T \frac{dT}{T^2}\int_0^T (C_{p\,(solid)} - C''_{p\,(solid)})dT + i - i',$$

since $\rho_0 = A_0 - A_0'$ represents the transition or melting heat at the absolute zero. Now the application of the Nernst Heat Theorem requires for the direct interconversion of condensed systems that the integration constant disappears; therefore, i must equal i', *i.e., the value of the chemical constants is independent of the nature of the solid body* (see translators' note, page 190).

226. Numerical Calculation of Gaseous Equilibria.—The practical application of Eq. (234*d*) takes the following form. First, H_0' is determined[1] by means of Eq. (212). The individual values for i_1, i_2, etc., which unite to form J, are taken from Table 24, and the integral Ψ is evaluated either by direct calculation from tables or by graphic methods. Now for the rigid calculation of the H_0' values as well as the integral Ψ, the specific heats of the gases must be known accurately down to the absolute zero. In general, however, this is not possible, so that the true value of H_0' cannot be determined. But in spite of this the calculation can be carried out, *if all claims to the true value of H_0' are renounced.* Then it is only necessary to see that the same value is used for H_0' in Eq (234*d*), even though it is fictitious, as was used for the estimation of the i value from the vapor-pressure curve. Therefore, the corresponding (fictitious) values of C_{p0} are given next to the i values in Table 24.[2]

Henceforth, an application of Eq (234*d*) to the NH_3 equilibrium raises no difficulties of any sort in connection with Eq (212*a*) We obtain

$$\log K_p = -\frac{18{,}810}{4.571T} + \frac{11.76}{1.985}\log T - \frac{0.00077T}{4.571} - \frac{1.7 \cdot 10^{-6}T^2}{4.571}$$
$$- 3 \cdot 3.80 + 0 + 2 \cdot 2.2$$
$$= -\frac{4111}{T} + 5.93 \log T - 0.000015T - 0.37 \cdot 10^{-6}\, T^2 - 6.7.$$

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[1] The index g will be dropped in what follows

[2] It may be assumed with considerable confidence that all gases lose their energy of rotation at sufficiently low temperatures, and, therefore, attain a molecular heat of $C_p = \frac{3}{2}R$, *i.e.*, become thermally monatomic, and, therefore, i can be theoretically determined at very low temperatures according to Eq (133*a*), valid for monatomic substances. However, this calculation is for the present without significance at higher temperatures, since the increase in the heat of rotation C_{pr} is not known, and therefore it is impossible to evaluate the integrals Φ and Ψ for the heat of rotation.

TABLE 53.—EQUILIBRIUM CONSTANT K_p OF AMMONIA FOR DIFFERENT TEMPERATURES

T	*log* K_p calc.	*log* K_p obs
773	4 80	
834	5 33	5 34
904	5 89	5 886
995	6 45	6 47
1074	6 91	6 90
1187	7 43	7 40

In the preceding table several of the values for K_p calculated in this manner are compared with the values measured directly by Haber. The applicability of the formula proves to be very satisfactory. In judging the results, it must be borne in mind that the chemical constant of NH_3 is not calculated from the vapor-pressure formula, but back from the NH_3 equilibrium.

When gaseous equilibria at temperatures higher than 1200° *abs.* are investigated, the change in the specific heats of the gases H_2, N_2, O_2, etc. with temperature must be borne in mind. As an example of the manner of carrying out this calculation, consider the water-vapor equilibrium $2H_2 + O_2 \rightleftarrows 2H_2O$.

There is given·

$$H' = 115{,}060\ cal \text{ at } 273°$$

$$H_2: C_p = 6.96 + \varphi\left(\frac{5000}{T}\right)$$

$$O_2 .\ C_p = 6\ 96 + \varphi\left(\frac{4100}{T}\right)$$

$$H_2O.\ C_p = 7\ 95 + \varphi\left(\frac{2260}{T}\right) + 2\varphi\left(\frac{5000}{T}\right),$$

where $\varphi\left(\frac{\Theta}{T}\right)$ represents the Planck-Einstein function Eq (98*a*). The *i* values are again taken from Table 24

Since the function φ is of no importance at low temperatures, we obtain then for the absolute zero.

$$H_0' = 115{,}060 - \frac{(2\ \ 6\ 96 + 6\ 96 - 2\ \ 7.95)273}{1360} = 113{,}700\ cal.$$

Therefore,

$$log\ K_p = -\frac{113{,}700}{4\ 571T} + \frac{4\ 86}{1\ 985}\, log\ T + \frac{1}{4571}\int_0^T \frac{dT}{T^2}\int_0^T\left[2\varphi\left(\frac{5000}{T}\right) + \varphi\left(\frac{4100}{T}\right) - 2\varphi\left(\frac{2260}{T}\right) - 4\varphi\left(\frac{5000}{T}\right)\right]dT - 7\ 4 + 0.7 + 4.2$$

and for the special case of 1000°,

$$(log\ K_p = -24.97 + 7\ 50 + \frac{1}{4\ 571}(0.026 + 0.036 - 0.44 - 0.052)$$
$$-2.5 = -19.96,$$

if the integral is evaluated according to Table 52.

The computation for several other temperatures leads to the Table 54, in which the degree of dissociation α (for $p = 1$) obtained according to Eq. (181*b*) by means of the calculated K_p values are placed next to the α values directly observed.

TABLE 54.—DISSOCIATION OF WATER VAPOR

T	$\log K_p$	100α calc	100α obs	Method
290	-82.21	$0.495 \cdot 10^{-25}$	$0.47 \cdot 10^{-25}$	H_2, O_2 cell (**217**)
1000	-19.96	$2.8 \cdot 10^{-5}$		
1397	-12.63	$7.8 \cdot 10^{-3}$	$7.8 \cdot 10^{-3}$	Streaming method (**179**)
1705	-9.29	$10.2 \cdot 10^{-2}$	$10.2 \cdot 10^{-2}$	Semi-permeable membrane (**41**)
2155	-6.09	1.18	1.18	Semipermeable membrane (**41**)
2505	-1.42	1.15	1.5	Explosion method[1]
2731	-3.55	7.9	8.2	Explosion method[1]

[1] For the application of the explosion method, briefly discussed in **55**, to the estimation of chemical equilibria at higher temperatures, see SIEGEL, *Z. physik. Chem.*, **87**, 641 (1914). This paper cites the older literature.

227. Heterogeneous Equilibrium.—It is easy to show that Eq. (231*d*) as well as the L. M. A. and Eq. (214*a*) also hold for heterogeneous equilibria under the following conditions: the partial pressures (in K_p), the chemical constants, and the expression $C'_{p_0} \log T$ of all substances present at the same time as solid phases are lacking; the integral Ψ contains the molecular heats of the solid bodies as far as these are present as well as the C''_T value of the gases; H' represents the heat content of reaction observed directly in the heterogeneous system.

The dissociation of calcium carbonate serves as an example of a univariant system in which the partial pressure of the carbon dioxide (p_{CO_2}) enters in place of K_p.

The heat content of reaction amounts to 39700 ± 700 *cal* at $T = 290°$.[1] The C'_p values for the solid carbonate and oxide, as well as the integrals derived from them, are taken with slight changes from Miething's tables. It is assumed for gaseous carbon dioxide that[2]

$$C_p = 6.96 + 2\varphi\left(\frac{960}{T}\right) + 2\varphi\left(\frac{3400}{T}\right)$$

We first obtain:

$$\begin{aligned} H_0' &= 39700 + T\Phi_{CaO} - 6.96T - T\Phi_{CO_2} + T\Phi_{CaCO_3} \\ &= 39700 - 1530 - 2020 - 150 + 3500 = 39500 \textit{ cal.} \end{aligned}$$

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[1] See VON KOHNER, "Dissertation," Berlin (1914).

[2] See EUCKEN, A., *Z. physik. Chem.*, **100**, 159 (1922).

Finally

$$\log K_p = \log p_{CO_2} = -\frac{39500}{4\ 571T} + \frac{6\ 96}{1\ 985}\log T + \frac{1}{4\ 571}\int_0^T \frac{dT}{T^2}\left\{\int_0^T C'_{p\,CaO}dT + 2\int_0^T \varphi\left(\frac{960}{T}\right)dT + 2\int_0^T \varphi\left(\frac{3400}{T}\right)dT - \int_0^T C_{p\,CaCO_3}dT\right\} + 0.80.$$

Since Miething's tables extend only to $T = 600°$ for $CaCO_3$, and only to 700° for CaO and the lowest temperature for which a dissociation pressure for $CaCO_3$ has been measured is 787°, it is necessary to undertake an extrapolation. We set 5 87 for the integral for $CaCO_3$ at 787° and 2 37 for CaO, from which it follows from the formula for the dissociation pressure that $p_{CO_2} = 6\ 10^{-4}$, while the measurements give the value $3\ 8\ \ 10^{-4}$ *atm.* (see Table 42). In consideration of the uncertainty with which the values in the calculation are affected the agreement may be considered satisfactory.

The combustion of solid carbon to gaseous CO_2 may be chosen for a divariant system The calculation is carried out for the diamond, as its specific heat is better known than that of amorphous carbon. Since the effect of the greater heat of combustion of amorphous carbon and its greater specific heat compared to the diamond partially compensate, the calculation of the final result for the diamond will not be far from that for amorphous carbon

Here

$$H' = 94{,}300\ cal \text{ at } 290° \text{ for } C_p \text{ (graphite).}$$

(See Table 2 in Miething's tables)

$$O_2\quad C'_p = 6\ 96 + \varphi\left(\frac{4100}{T}\right)$$

$$CO_2\quad C'_p = 6\ 96 + \varphi\left(\frac{960}{T}\right) + 2\varphi\left(\frac{3400}{T}\right)$$

$$\underbrace{H_0' = 94{,}300 - 238 - \underbrace{6\ 96\ \ 290}_{2000} + \underbrace{6\ 96\ \ 290}_{2000} + 2\underbrace{\int_0^T \varphi\left(\frac{960}{T}\right)dT}_{150}}_{94200}$$

$$\log K_p = \log\frac{p_{O_2}}{p_{CO_2}} = -\frac{94{,}200}{4\ 571T} + \frac{1}{4\ 571}\int_0^T \frac{dT}{T^2}\left\{\int_0^T C'_{pC}dT + \int_0^T \varphi\left(\frac{4100}{T}\right)dT - 2\int_0^T \varphi\left(\frac{960}{T}\right)dT - 2\int_0^T \varphi\left(\frac{3400}{T}\right)dT\right\} + 0.7 - 0.80.$$

Computation for $T = 1300°$ gives

$$\log Kp = -15\ 85 + 0\ 80 + 0\ 020 - 0.565 - 0.066 - 0.10 = -15.77.$$

Here the agreement with the experimentally determined $\log K_p = 15\ 54$ (see page 355) is such that the difference can be explained simply by the considerable uncertainty with which the individual numerical values appearing in the equation as well as in the experimentally determined K_p value are affected at 1300° However, in this example the first member is of very much more importance than all the rest, which for the greater part compensate one another. At room temperature the first member is of still more importance than at higher temperatures, for $T = 290°$ we obtain

$$\log K_p = -71\ 11 + 0\ 11 - 0\ 03 - 0\ 10 = -71\ 13$$

At this temperature only a vanishingly small fraction of the oxygen remains unburned in the union of carbon with oxygen

228. Derivation of an Approximation Formula.—While the heat of reaction of H' can, as a rule, be assumed as known, the molecular heats as well as the chemical constants are lacking for numerous substances. In such cases any claim to an exact solution of the problem must naturally be renounced. However, by introducing some simplifications, Nernst was able to put Eq. (234*d*) in the form of an approximation formula, which, as a rule, yields the correct order of magnitude of the equilibrium constant K_p and, therefore, gives an idea of the stability relations of the equilibrium.

The simplifications are as follows.

1. The heat of reaction H' measured at room temperature is used directly in place of H_0'.

2. The following are put in place of the true molecular heats: the value 3.5 for every gas molecule and the value 0 for all solid and liquid substances. The term $\frac{1}{R}\int \frac{dT}{T^2}\int_0^T \Sigma C'_p dT$, therefore, is eliminated and the term with $\log T$ reads:

$$\Delta n \frac{3\ 5}{1.985} \log T \sim \Delta n\ 1\ 75 \log T,$$

in which the expression Δn represents the difference in the number of gas molecules disappearing minus the number of those appearing.

TABLE 55 [1]—CONVENTIONAL CHEMICAL CONSTANTS *i*

H_2..	1 6	HCl......	3 0	CS_2	3 1
CH_4......	2 5	HI......	3 4	NH_3	3 3
N_2..	2 6	NO.	3 5	H_2O	3 6
O_2	2 8	N_2O.......	3 3	CCl_4. ...	3 1
CO.	3 5	H_2S....	3 0	$CHCl_3$.......	3 2
Cl_2. ...	3 1	SO_2..	3 3	C_6H_6. .. .	3 0
I_2. .	3 9	CO_2.... .	3 2		

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[1] For the atoms H_1, N_1, etc , half the value given for the molecules is to be substituted

3. In order to compensate as far as possible for the simplifications (1) and (2) the conventional chemical constant ι' will be used, which may be empirically estimated from gaseous equilibria (see Table 55) in place of the true values of ι determined by the vapor-pressure formula (Eq. (131f)). Therefore, in place of Eq (234d, page 411) we obtain:

$$log\ K_p = -\frac{H'}{4.571T} + \Delta n\ 1.75\ log\ T + \Sigma\iota'. \qquad (239)$$

The value of 3.5 given above for the molecules of gaseous substances is arbitrary[1] within certain limits; however, it seems rather better to retain the historical value 3.5, as it is doubtful whether a change in this value would lead to an improvement of the formula. In all cases it is to be observed that every change in Eq. (239) also requires a similar change in the empirically determined conventional chemical constant ι'.

229. Application of the Approximation Formula.—As the influence of the expressions $\frac{\Sigma C'_{p0}}{1.985}\ log\ T$ and $\int\frac{dT}{T^2}\int\Sigma C'_p dT$, which have undergone the most simplification, decreases, Eq. (239) becomes more serviceable. This is (*cet. par.*) all the more true the smaller the difference between the disappearing and appearing number of moles of gas molecules. Equation (239), therefore, yields relatively exact values for reactions in which $\Delta n = 0$, *i.e.*, in which the mole number remains constant. It is still applicable for $\Delta n = \pm 1$, but it should be used with caution in case $\Delta n < -1$ or $> +1$.[2]

A number of examples, the greater part of which are taken from the excellent monograph of Pollitzer, are given here as proofs:

1. $\Delta n = 0.$

Table 56 shows very clearly that K_p increases more markedly with increasing temperature the greater the heat content of the reaction, as predicted by Eq. (231), but at the same time it shows that the magnitude of the heat of reaction also influences the absolute value of K_p and, indeed, a large heat content of reaction corresponds to a small K_p, a result which is quite obvious, since

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[1] See p. 283 of the monograph of Pollitzer and Nernst for the reasons which led to this choice.

[2] This classification presupposes that no fractions of one mole appear in the reaction equation.

TABLE 56.—EQUILIBRIUM CONSTANTS K_p OF SOME REACTIONS PRECEDING WITHOUT CHANGE IN MOLE NUMBER

Reaction	H'	$\Sigma n_i'$	300°		1000°		2000°	
			log K_p obs[1]	log K_p calc	log K_p obs	log K_p calc	log K_p obs	log K_p calc
$I_2 + H_2 = 2HI$	2760	−0 7	− 2 88	− 2 7	− 1 34	− 1 3		−1 0
$CO + H_2O = H_2 + CO_2$	10420	+2 3		− 5 3	− 0 17	+ 0 03		+1 165
$H_2 + Br_2 = 2HBr$	24200	−1 6	−18 55	−19 25	abt − 6 5	− 6 9		−4 25
$2NO = N_2 + O_2$	43200	+1 6		abt −30 0		− 7 85	abt. −3 6	−3 12
$H_2 + Cl_2 = 2HCl$	44000	−1 3	−33 2	−33 38	−10 43	−10 93	−5 77 (at 1829°)	−6 11 (at 1829°)

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[1] From e m f measurements

a large heat content of reaction points to a firm combination of the molecules formed.

The influence of the chemical constants is greater the smaller the term $\frac{H'}{4.571T}$ and therefore the higher the temperature and the smaller the heat content. An application of Eq. (239) to very high temperatures would lead to the result that K_p is nearly independent of the temperature. However, this conclusion is in no way binding, since it is just at high temperatures that the terms, which are completely neglected and which contain the molecular heats, must become most prominent.

The combustion of carbon to carbon dioxide, which has already been treated exhaustively, serves as an example of a heterogeneous reaction which proceeds without change in the number of moles of the gases The calculations carried out in **227** show the small influence of the terms which contain the specific heat and therefore the justification for applying (Eq (239)) directly.

2. $\Delta n = +1$

Since also in numerous cases the conventional chemical constants are not known, it is necessary to introduce a unit value for i' in Eq (239). The value chosen as such as $i' = 3$ for molecules and $i' = 1.5$ for atoms. Equation (239) then takes the form:

$$\log K_p = -\frac{H'}{4.571T} + 1.75 \log T + 3 \quad (\text{or } +1.5) \qquad (239a)$$

according as dissociation takes place into molecules or atoms.

In order to facilitate a comparison between observation and the results of Eq. (239*a*), it is expedient to compare the observed temperature T_k with the calculated for a given K_p value instead of the K_p values. $K_p = \frac{1}{3}$ was chosen as a normal value which corresponds to 50 per cent dissociation for a total pressure of 1 *atm*. in a reaction according to the scheme $A + B \rightarrow AB$, and to about 27.7 per cent for a reaction according to the scheme $2A \rightarrow A_2$ (see Eqs. (180*a*) and (178*c*)).

The applicability of the approximation formula also proves to be thoroughly satisfactory here. For the dissociation of diatomic gases into their atoms this result is due only to the choice of 1.5 for the i' value of the atoms. Moreover, as a rule, the application of the exact formula (Eq. (234*d*)) involves

TABLE 57.—DISSOCIATION TEMPERATURES OF SOME GASES DISSOCIATING INTO TWO MOLECULES OR TWO ATOMS

Reaction	H'	T_k obs	T_k calc.
$2NO_2 = N_2O_4$......	12450	327	344
$2HCOOH = (HCOOH)_2$ ..	14780	410	410
$2CH_3COOH = (CH_3COOH)_2$..	16600	425	450
$PCl_3 + Cl_2 = PCl_5$.	18500	480	500
$H_2O + SO_3 = H_2SO_4$.	21850	623	599
$2I = I_2$	35000	1310	900
$2Br = Br_2$.	47000	1650	1150
$2Cl = Cl_2$	56000	about 1980	1900
$2H = H_2$	about 95000	about 3350	3150

relatively few difficulties in the dissociation into atoms, since the specific heats for the atoms as well as the chemical constants on the basis of Eq. (133*a*) may be assumed as known. For example, one obtains the formula

$$log\ K_p = \frac{95000}{4.571T} + 1.50\,log\ T - \frac{1}{4.571}\int_0^T \frac{dT}{T^2}\int_0^T \varphi\left(\frac{5000}{T}\right)dT + 0.50$$

for the dissociation of hydrogen according to Eq. (234*d*) for the values $H_0' = 95000$; $C'_{pH} = 4\ 96$; $C'_{pH2} = 6\ 96 + \varphi\left(\frac{5000}{T}\right)$, $i_H = 1.60$; $i_{H_2} = -3.70$ (according to Table 24), which yields $K_p = 0.3$ at 3350° (instead of $K_p = \frac{1}{3}$) in excellent agreement with the observed value.

Of the heterogeneous reactions which proceed with the formation of a mole of a gas, the dissociation of a number of carbonates may be considered. Here $i'_{CO_2} = 3.2$ according to Table 55 and

$$log\ K_p = log\ p = \frac{-H'}{4\ 571T} + 1.75\ log\ T + 3.2.$$

If we desire the temperature T at which 1 *atm.* pressure is reached ($log\ p = 0$), we get the relation:

$$\frac{H'}{T} = 4.571(1.75\ log\ T_1 + 3.2),$$

which reminds us of Eq. (125*a*).

The decomposition temperatures calculated from this are given in the following table:

TABLE 58.—DISSOCIATION TEMPERATURES OF SOME CARBONATES UNDER ATMOSPHERIC PRESSURE

Carbonate	H'	T calc	T obs.
Ag_2CO_3	22060	548	498
$PbCO_3$.	22580	610	575
$MnCO_3$	23500	632	abt 600
$CaCO_3$. . .	39700	1030	1181
$SrCO_3$. .	55770	1403	1428

The agreement is satisfactory except for calcium carbonate. That the results in Table 58 are more satisfactory than those in Table 57 depends primarily upon the fact that in this case we are concerned with the dissociation of the same gas (CO_2), so that the uncertainties involved in the chemical constants are eliminated to a large extent.

3. $\Delta n \geqq 2$.

Somewhat greater caution is necessary in the application of Eq. (239) to reactions in which more than two gas molecules appear or disappear, since, as mentioned before, the simplified second member becomes of more importance than if Δn is equal to 1 or 0.[1]

If the values of the chemical constants are not accurately known and are to be estimated only by rough appraisal, the approximation formula may also yield values which are at least qualitatively correct estimates for the position of the equilibrium when $\Delta n \geqq 2$. For example, some observations have been made that the dissociation of heavy metal nitrates into oxides and NO or NO_2 and O_2[1] proceeds with a very much higher heat of reaction than the dissociation of the carbonate, although a dissociation pressure of 1 *atm.* is reached at approximately the same temperature with the nitrates as with the carbonates. The explanation is that in the dissociation of the nitrate the number of gas molecules resulting is greater than in the dissociation of the carbonate; accordingly, the second and third members of Eq. (239) become of distinctly more importance than for the carbonates. In this manner, the first term, which is greater owing to the higher heat of reaction, is compensated in the nitrates, so that, finally, at the same temperature about the same value of K_p results as in the dissociating carbonates which have the smaller heats of reaction and for which the term Δn 1.75 $\log T$ is of lesser importance.

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[1] Since the greater number of the conventional chemical constants given in Table 55 have been estimated empirically by the aid of Eq. (239), from only a single known equilibrium, the application of this equation to the same equilibrium does not lead to a result which can be used to judge the formula with respect to the absolute value of K_p. This explains why almost the same value is obtained for K_p in the ammonia equilibrium by means of Eq. (239) and the i' values given in Table 55 as with the exact formula (Eq. (234)).

II. CHEMICAL REACTION VELOCITY

1. EMPIRICAL PRESENTATION OF THE FUNDAMENTAL LAWS

a. Homogeneous Systems

230. General.—As has already been shown in **8**, the consideration of the time course of a reaction leads to the introduction of the idea of chemical-reaction velocity which was defined there as the change in the quantity or the concentration of the reacting substances in unit time $\frac{dn}{dt}$ or $\frac{dc}{dt}$.

The example mentioned in **11** and **13** from the field of radioactivity treats the simplest conceivable case of a reaction, since the initial material consists of a single substance. Now the task of the remainder of this section will consist in extending the considerations stated above to complicated reactions and learning more about the properties of the constants determining chemical-reaction velocity. In order to have the simplest possible relations it will first be assumed that the course of the reactions be entirely in one direction, *i.e.*, the exchange proceeds completely in one direction just as in a radioactive decomposition. This hypothesis may always be considered as practically fulfilled so long as the chemical system under consideration is still far from its position of equilibrium. The results so obtained may be applied to the course of the reaction in the neighborhood of the equilibrium point without difficulty (see **233**).

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[1] For example, lead nitrate decomposes according to the equation $Pb(NO_3)_2 = PbO + 2NO_2 + \frac{1}{2}O_2$.

231. Unimolecular Reactions.—The inversion of cane sugar ($C_{12}H_{22}O_{11} + H_2O = 2C_6H_{12}O_6$) serves as an example of a reaction which starts with a single molecular species and may, therefore, be designated as unimolecular. In this case one biose molecule (cane sugar) is split up into two monoses (fructose and glucose) by the addition of water. Strictly speaking, there are two initial substances (cane sugar and water), though, in general, the water exists in such great excess that its effect upon the course of the entire reaction remains practically constant and therefore the (relative) reaction velocity depends only upon the number of cane sugar molecules existing at the moment or upon the momentary concentration of the cane sugar. Therefore, just as in **11**,

$$-\frac{1}{c}\frac{dc}{dt} = k \quad \text{or} \quad \frac{-dc}{dt} = kc. \qquad (240)$$

Now the concentration x of one of the monoses may be introduced in place of the concentration c of the cane sugar. Since one mole of monose always results from one mole of cane sugar, the sum of the momentary concentrations of the cane sugar and of one of the monoses must remain constant and be equal to the initial concentration a of the cane sugar, therefore,

$$c + x = a \quad \text{or} \quad a - x = c \quad \text{and at the same time} \quad \frac{dc}{dt} = -\frac{dx}{dt}.$$

Equation (240) may, therefore, also be written as follows:

$$\frac{dx}{dt} = k(a - x), \qquad (240a)$$

whose integration gives.

$$t = \frac{1}{k}\ln\frac{a}{a - x}, \qquad (240b)$$

when it is kept in mind that $x = 0$ when $t = 0$.

The course of the inversion of cane sugar may be followed very easily and accurately experimentally, since the dissolved cane sugar and the mixture of the resulting monoses, which is designated as "invert sugar," rotate the plane of polarized light in different directions. One per cent sugar solution rotates polarized sodium light about $\alpha_0 = +0.665°$ (to the right) for a tube of 10 *cm.* length, while a 1 per cent invert sugar solution rotates about $\beta_0 = -0.215°$ (to the left). In case the solution contains c per cent cane sugar and x per cent invert sugar per liter, the total rotation observed is

$$\alpha = c\alpha_0 + x\beta_0 = a\alpha_0 - x\alpha_0 + x\beta_0 = a\alpha_0 - x(\alpha_0 - \beta_0) \text{ angular degrees,}$$

from which x can be calculated and substituted in Eq. (240*b*). Keeping in mind that the initial rotation, directly observed, amounts to $\alpha_0' = a\alpha_0$ and the rotation at the end of the reaction amounts to $\beta_0' = a\beta_0$, we obtain finally in place of Eq. (240*b*) that

$$t = \frac{1}{k} ln \frac{a}{\frac{\alpha_0'}{\alpha_0} - \frac{\alpha_0' - \alpha}{\alpha_0 - \beta_0}} = \frac{1}{k} ln \frac{\alpha_0' - \beta_0'}{\alpha - \beta_0'}, \qquad (240c)$$

an equation in which, except for t and k, we have only the angles which are to be read on the polarization apparatus.[1]

If the values of k in such an inversion experiment are calculated from the individual t and α values corresponding to it, then k must be constant for the entire series of readings. The following table, which is taken from the first exact investigation of the cane sugar inversion (Wilhelmy, 1850), shows that this requirement is, in fact, fulfilled in a satisfactory manner:

TABLE 59.—COURSE OF A CANE SUGAR INVERSION

t, minutes	α	$\alpha - \beta_0'$	$k = \frac{1}{t} log \frac{\alpha_0' - \beta_0'}{\alpha - \beta_0'}$
0	46.75° (α_0')	65.50 ($\alpha_0' - \beta'_0$)	
30	41.00	59.75	0.00133
90	30.75	49.50	0.00135
150	22.00	40.75	0.00132
330	2.75	21.50	0.00146
630	−10.00	8.75	0.00139
∞	−18.75 (β_0')		

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[1] It will be recognized that $\alpha_0' - \beta_0'$ represents the total rotation from the initial to the final value, since the quotient $\frac{\alpha_0' - \beta_0'}{\alpha - \beta_0'}$ must enter in place of the quotient $\frac{a}{a - x} = \frac{a}{c}$ in Eq. (240*b*), therefore, the initial concentration a corresponds to $\alpha_0' - \beta_0'$ and a given concentration c to $\alpha - \beta_0'$.

232. Reactions of Higher Order.—In order to obtain an expression for a more complicated reaction we can proceed likewise from Eq. (240). If a reaction of the scheme

$$[A] + [B] + [C] \rightarrow [A'] + [B'] + [C'] \ . \ . \ .$$

is considered it can be reduced to the simple scheme $[A] \rightarrow [A'] + [B'] \ . \ . \ .$, in which first [A], then [B], and then [C] is kept constant in individual experiments by means of suitable experimental precautions. This can be achieved most simply by putting in the reaction chamber a great excess of those substances whose concentration we wish to hold constant.[1] If we hold the concentration of the substances [B] and [C] constant one time and then that of the substances [A] and [C], etc., we find the series:

1. Reaction velocity = k_1 [A].
2. Reaction velocity = k_2 [B]
3. Reaction velocity = k_3 [C].

These equations, which hold for the same reaction, can be united with one another when the following is set, in general, for the variables [A], [B], and [C]:

$$\text{Reaction velocity} = k[A]\,[B]\,[C].$$

The three special cases given above follow unequivocally from this and only this equation. For example, in the first special case in which [B] and [C] remain constant, k is to be set equal to k[B] [C]. Since the conversion of the substances proceeds in equivalent quantities, it is immaterial whether the reaction velocity is expressed by the decrease of [A], [B], or [C] with time or by the increase of the concentration of one of the reaction products, *i.e.*,

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} \ . \ . = +\frac{d[A']}{dt} = +\frac{d[B']}{dt} = k[A]\,[B]\,[C]. \quad (241)$$

Ester saponification, namely,

$$\underset{\text{Ester}}{RCOOR'} + OH^- \rightarrow \underset{\text{Anion}}{RCOO^-} + \underset{\text{Alcohol}}{R'OH}, \quad (242)$$

may be briefly discussed as an example of a higher-order reaction proceeding in one direction where R and R' may signify different or similar organic radicals. When the initial concentration of the ester is set equal to a, the OH^- ions to b, and the concentrations of the anion and of the alcohol to x we have:

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[1] This case has already been realized in the cane sugar inversion, here the water always exists in such great excess that its concentration remains practically constant.

$$\frac{dx}{dt} = k[RCO_2R'][OH^-] = k(a - x)(b - x). \qquad (243)$$

For integration this equation takes the form

$$k\,dt = \frac{dx}{(a - x)(b - x)} = \frac{dx}{a - b}\left(\frac{1}{b - x} - \frac{1}{a - x}\right),$$

from which it follows, analogous to Eq. (240a), that

$$kt = \frac{1}{a - b}\left(\ln\frac{b}{b - x} - \ln\frac{a}{a - x}\right) = \frac{1}{a - b}\ln\frac{b(a - x)}{a(b - x)}. \qquad (243a)$$

The experimental verification of Eq. (243a) for the reaction of ester saponification may be carried out in different ways. An especially simple and satisfactory procedure depends upon the change in electrical conductivity of the mixture. The conductivity decreases during the reaction, since the speedy OH^- ion is exchanged for the slower anion of the organic salt. Just as the concentrations in the final formula for the sugar inversion can be completely replaced by the angles of rotation, so may the initial conductivity, the final conductivity, and the momentary conductivity of the mixture be introduced in Eq. (243a) in place of the concentrations a, b, x, at least for the case where the OH^- ions exist in excess.

When the ester and the OH^- ions are present in equimolecular quantities at the start, Eq. (243) reduces to $\frac{dx}{dt} = k(a - x)^2$, which permits of integration by Eq. (14a) if $a - x = y$ is substituted and, therefore, $dx = -dy$. In this way

$$\frac{1}{y} = \frac{1}{a - x} = kt + Const.$$

is obtained or, since $x = 0$ when $t = 0$,

$$kt = \frac{1}{a - x} - \frac{1}{a} = \frac{x}{(a - x)a}. \qquad (243b)$$

233. Incomplete Reactions.—The treatment of reactions which do not proceed to completion in one direction depends upon the assumption that the reaction

$$[A] + [B] + [C] \ldots \rightarrow [A'] + [B'] + [C'] \ldots \qquad (I)$$

and the counter reaction

$$[A'] + [B'] + [C'] \ldots \rightarrow [A] + [B] + [C] \ldots \qquad (II)$$

proceed essentially independent of one another. The increase, say, of the substance [A′] therefore amounts, according to reaction (I), to

$$\left[\frac{d[A']}{dt}\right]_1 = k_1[A]\,[B]\,[C] \qquad ,$$

but according to the counter reaction (II) the decrease in concentration of [A′] at the same time is

$$-\left[\frac{d[A']}{dt}\right]_2 = k_2[A']\,[B']\,[C'] \quad . \quad . \quad .$$

Therefore, the increase of [A′] amounts *in toto* to

$$\frac{d[A']}{dt} = k_1[A]\,[B]\,[C] - k_2[A']\,[B']\,[C'] \qquad (244)$$

The rate of change $\frac{d[A']}{dt}$ decreases with time and finally becomes equal to zero, the composition of the mixture then remaining constant. The system has reached its equilibrium state. The following, therefore, holds for the chemical equilibrium:

$$\frac{d[A']}{dt} = k_1[A]\,[B]\,[C] - k_2[A']\,[B']\,[C'] = 0 \text{ or } \frac{[A]\,[B]\,[C]}{[A']\,[B']\,[C']} = \frac{k_2}{k_1}.$$

Since the L.M.A.[1] in the present case possesses the form $\frac{[A]\,[B]\,[C]}{[A']\,[B']\,[C']} = K$ it follows that

$$\frac{k_2}{k_1} = K, \qquad (245)$$

i e, the equilibrium constant K of the L.M.A. is represented by the ratio of the velocity constants of the reaction for the two opposing

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[1] * The author's form of expressing the law of mass action in terms of stoichiometric concentrations instead of in terms of activities has been retained for the discussion of reaction velocity. This procedure is justified for the cases under consideration where all the components obey the gas laws with only negligible deviation However, when ionic species are involved the activity should be used whenever an equilibrium state is involved in some stage of the process. For details regarding the important question of the use of activities and of stoichiometric concentrations in the study of reaction velocity reference should be made to the recent papers by **Bjerrum** (*Z. physik. Chem*, **108**, 82 (1924)) and by **Bronsted** and **Teeter** (*J. Phys. Chem*, **28**, 579 (1924)) where references to earlier papers of Harned and others are given and where the various modifications of positive and negative salt catalysis are discussed. See also **Bronsted**, *Z. physik. Chem*, **115**, 337 (1925).

directions. If, therefore, K has a very small value, as in the water-vapor equilibrium at room temperature (see Table 54), this states that the velocity of formation k_1 has under all circumstances a very much higher value than the velocity of decomposition k_2

The important relation (Eq. (245)) depends, on the one hand, upon the law of mass action and, on the other hand, upon Eq. (241) for the reaction velocity, both of which may be considered as completely established empirically from numerous studies on different reactions. In spite of this, it is of interest that in certain cases Eq (245) can be established directly.

For example, Knoblauch[1] succeeded in measuring both velocity constants k_1 and k_2 as well as K for the reaction:

$$CH_3CO_2C_2H_5 + H_2O \rightleftarrows CH_3COOH + C_2H_5OH \qquad (242a)$$

He found the velocity constants k_1 and k_2 to be 0 0000815 and 0 000238 respectively when measured individually at a great distance from the equilibrium point where the counter reaction is of no measurable importance. The ratio of $\frac{k_2}{k_1}$ is 2.92, which was in very satisfactory agreement with the value of the equilibrium constant $K = 2\,84$ at 20°.

234. The Temperature Coefficient of Reaction Velocity.—Up to this point no further specifications of any kind have been made concerning the value k appearing in the basic equation of chemical kinetics (Eq. (241)), except that it was assumed that k represented a constant so long as the conditions of the experiment remained the same during the reaction. However, different values for k are obtained if some of the conditions of the experiment are changed. First of all, temperature exercises a very considerable influence in numerous homogeneous reactions. Reactions in which the temperature coefficient is small do not often proceed in a truly homogeneous manner. As shown by the following table, the reaction velocity in the majority of homogeneous reactions increases two-to fourfold for a temperature increment of 10°, and occasionally in biochemical reactions sevenfold.

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[1] *Z. physik Chem*, **22**, 268 (1897)

TABLE 60—RATIO OF THE VELOCITY CONSTANTS FOR A TEMPERATURE INCREASE OF 10°

Reaction	$\frac{k_{T+10}}{k_T}$
$PH_3 \rightarrow \frac{1}{4}P_4 + \frac{3}{2}H_2$	1.8
$CH_3CO_2C_2H_5 + NaOH$	1.89
$KClO_3 + FeSO_4 + H_2SO_4$	2.44
$NaOC_2H_5 + CH_3I$	3.34
Sugar inversion	3.63
$COS + H_2O$	3.68
Enzyme action	7.14

Assuming $\frac{k_{T+10}}{k_T} = 3$ as an average, this means that the velocity of a homogeneous reaction is increased or diminished about 3^{10} fold, *i.e.*, about 100,000 fold for temperature change of 100° or about 10^{10} fold for a temperature change of 200°. These values are in good agreement with general chemical experience, for numerous reactions proceeding briskly at higher temperature come to a practically complete standstill by cooling a few hundred degrees.

Different empirical formulas have been proposed for the accurate representation of the temperature coefficient of the k values.[1] According to Arrhenius, the equation

$$\log k = -\frac{A}{T} + B, \qquad (246)$$

which contains only two constants, A and B, is applicable in a number of cases. The decomposition of monochloracetic acid to glycollic and hydrochloric acids may be offered as an example of the usefulness of Eq. (246).[2]

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[1] A short summary of these is to be found in GOLDSCHMIDT, H., *Physik. Zeit.*, **10**, 207 (1909), also MELLOR, "Statics and Dynamics," Longmans, Green & Co. (1904).

[2] Investigated by Schwab. See VAN'T HOFF, "Etudes de dynamique chimique," p. 114.

TABLE 61.—DECOMPOSITION VELOCITY OF MONOCHLORACETIC ACID
$A = -5771$, $B = 16695$

T	k obs.	k calc
273 + 80	2.22	(2.22)
90	6.03	6.27
100	17.3	16.7
110	43.6	42.4
120	105	102
130	237	(237)

235. Kindling Temperature.—Due to the marked temperature coefficients of the velocity constants, the change in a mixture capable of reaction, such as oxyhydrogen gas, is often so minute at low temperatures that no progress is detectable in years. If the temperature is raised, the reaction velocity gradually assumes a perceptible value, and, owing to the heat of reaction, the temperature of the mixture is raised a little more. The further behavior of the mixture depends upon whether the major portion of the liberated heat of reaction is allowed to escape to the surroundings by radiation and heat conduction, or whether the loss of heat is so small in respect to the heat developed that the temperature keeps increasing further. In the first case, the reaction will proceed slowly, but will return again to a standstill if the temperature is lowered.

In the other case, reaction velocity always increases, due to the automatic temperature increase; therefore, the temperature increases further and the reaction velocity increases still more, so that it is completed in an exceedingly short time. The mixture kindles and burns or explodes. As a rule, at ordinary or low temperatures the losses of heat are very much greater than the minimum heat production from the minute reaction velocity.

If the mixture is heated the escape of heat usually increases, but the reaction velocity and, therefore, the heat production increase in a very much higher degree. Finally, a point is reached at which the heat production overbalances the loss, and at which the automatic increase of the temperature of the gas mixture begins; combustion, therefore, commences. This point is designated as the **kindling temperature.** Since this temperature is fixed by the conditions such that the quantity of heat given off to the surroundings in a unit of time is a little smaller than the quantity of heat developed within the mixture in the unit of time, it can be seen that the kindling temperature does not alone represent a chemical property of the gas mixture, but depends also upon some of its physical properties (such as heat conduction), as well as upon the experimental conditions (such as the size and the material of the experimental vessels). Since it is not possible to define the absolute kindling temperature of a gas mixture, only those kindling temperatures which are obtained by the use of a given method of procedure for different explosive gas mixtures can be compared. The following is a convenient method for the measurement of kindling temperatures An explosive gas mixture is rapidly and adiabatically compressed from an initial volume v_0 to a smaller value v by allowing a weight to fall upon the piston of the metal cylinder containing the gas. The temperature T at any instant may then be calculated from Eq (80). The occurrence of an explosion is shown by a violent backward thrust of the piston. By variation of v or T a point is reached at which an explosion still occurs. This represents the characteristic kindling temperatures for the procedure and mixture chosen.

Cassell[1] established the kindling temperatures for different oxyhydrogen gas mixtures according to this method by using a metal cylinder holding about 0.2 *l*. The results showed that a mixture of $2H_2$ and $3O_2$ possessed the lowest kindling temperature, about 670° *abs*

236. Propagation of Explosions.—If an explosive gas mixture is heated locally instead of throughout, the reaction, according to the extent to which the kindling conditions mentioned above are fulfilled, will either take place only at the point at which the heating occurs or will spread out through the entire gas mass from this point. The propagation of the reaction above the kindling temperature must obviously result in such a manner that the burning layer of the mixture heats the still unburned neighboring layers up to or above the kindling temperature

There are two varieties of propagation, according to the manner in which the heating is effected. In one kind the heating results solely through conduction of heat from layer to layer. Then the propagation velocity of the reaction is relatively small. It amounts at most to a few meters per second. This variety of burning is designated, as a rule, as a deflagration ("verpuffung"); also sometimes as an *explosion;* an example is the striking back of the flame in the tube of a Bunsen burner which is burning with too great an air supply.

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[1] *Ann. Physik.*, **51,** 685 (1916).

The second variety of heat transfer leads to a violent phenomenon which is designated as *detonation* If the reaction proceeds in a layer with a very high velocity and, therefore, endeavors to spread out quickly toward the sides, it will exercise a pressure upon its neighboring layers. Under some circumstances, the diffusion velocity of the reacting layer is so great that the neighboring layer cannot be turned aside and is, therefore, adiabatically compressed. The limiting velocity with which the particles of a body can still be elastically turned aside is the velocity of sound; the latter themselves are therefore brought to the kindling temperature and now act in turn in compressing the next layer adiabatically. The propagation velocity of such detonations is extraordinarily great and amounts to 2000 to 3000 *m.* per second, according to the nature of the gas mixture

As Dixon[1] showed, the detonation velocity is about equal to the velocity of sound in the burning gases at the explosion temperature itself. Since the velocity of sound increases proportionally to the square root of the absolute temperature, the detonation velocity is, in fact, considerably greater than the velocity of sound in the unburned gases at room temperature.

However, a sharp distinction cannot always be drawn between an explosion and a detonation. A detonation wave frequently develops by a gradual increase in velocity from an explosion.

237. Catalytic Phenomena.—In numerous cases the reaction velocity depends to a high degree upon substances which are added to the reaction mixture but which do not partake in the chemical exchange as judged by the usual gross reaction equation. Such substances are called **catalysts**; there are "positive catalysts" which accelerate the reaction, as well also as "negative catalysts" which retard the reaction. Out of the great mass of experimental material upon catalysis[1] only a few typical cases will be emphasized.

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[1] A summary of the experimental results of Dixon are to be found in *Ber. Deut. chem*, *Gesell.*, **38**, 2419 (1905), *also *J. Chem Soc*, **99**, 588 (1911).

H^+ ions exert an accelerating action upon a great number of reactions in organic chemistry, and it appears that the velocity constant is proportional to the H^+ concentration. The best-known examples of such reactions are the inversion of cane sugar and the saponification of esters by water (Eq. (245)).

The saponification of esters proceeds faster in alkaline as well as in acid solution than in the neighborhood of the neutral point. The reaction proceeds according to Eq. (242) in alkaline solution, *i.e.*, the velocity of saponification is directly proportional to the OH^- ion content. In acid solution Eq. (242*a*) holds; here the velocity is proportional to the H^+ ion concentration, owing to its catalytic action. However, the direct influence of the OH^- ions outweighs that of the H^+ ions as much as 1000 fold. Therefore, in a neutral solution, the action of the OH^- ions is practically the only one of importance.

In numerous gas reactions at high temperature, and especially combustions, the presence of traces of water vapor exerts a decisive influence. For example, it is impossible to make an absolutely dry mixture of the gases CO and O_2 explode A carbon monoxide flame, which is maintained by very dry carbon monoxide, burns in ordinary air, but is extinguished as soon as it is introduced into an atmosphere from which the water vapor has been carefully removed.

Where certain initial substances can react with one another in different ways, catalysts are frequently found, which noticeably accelerate only one of these reactions while other catalysts promote another reaction. Catalysts thus exhibit a specific action in these cases and the same initial mixture can be changed into entirely different end products. In biological chemistry such phenomena play a most important rôle. The catalysts acting specifically here are designated as ferments or enzymes. From a chemical standpoint they have been but little investigated. Most probably they are of very complicated molecular constitution The fermentation process serves as the best-known example of specific enzyme action; for example, certain types of sugars, trioses, hexoses, and nonoses are fermented by one enzyme, zymase, to alcohol and carbon dioxide and by another enzyme to lactic acid. The enzymes are closely related to the life functions of certain bacteria, although from the investigations of Buchner they can be separated from the bacteria without losing their activity.

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[1] See, for example, WOKER, GERTRUDE, "Die Katalyse," Stuttgart (1910); * RIDEAL and TAYLOR, "Catalysis in Theory and Practice," The Macmillan Company (1919).

An inorganic reaction in which a specific action of catalysts clearly appears is given by E. Abel.[1] The thiosulfate ion is oxidized to tetrathionate by hydrogen peroxide in the presence of iodide ions, but, on the contrary, to sulfate in the presence of molybdic acid.

If the same reaction proceeds in different solvents, then, in general, different values are found for the reaction velocity. For example, Menschutkin investigated the course of the reaction

$$N(C_2H_5)_3 + C_2H_5I = N(C_2H_5)_4I$$

in different organic solvents. He found Eq. (243a) holding for bimolecular actions to be confirmed in all cases, though the velocity constants increased from $k = 0.00018$ (in hexane) to 0.133 (in benzyl alcohol).

A general relation between the values of the velocity constants with other physical properties of the solvent which should be suitable for the theoretical explanation of the hitherto existing materials has not as yet been disclosed.

238. The Interpretation of Catalytic Actions by Means of Intermediate Reactions.—A greater part of the catalytic phenomena may be explained uniformly by the assumption of intermediate reactions. The conversion of initial substances into end products can follow different reaction paths. The reaction actually proceeds predominantly over the path which presents the least obstruction and therefore upon which the conversion will proceed the most rapidly. The way appearing most direct according to the gross reaction equation is frequently not the most rapid.

The so-called Landolt reaction[2] serves as a carefully investigated example of such a case:

$$5H_2SO_3 + 2HIO_3 \rightarrow 5H_2SO_4 + H_2O + I_2.$$

According to the gross reaction, one would expect that the sulfurous acid would be directly oxidized to sulfuric acid and therefore liberate iodine.

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[1] *Z. Elektrochem.*, **18,** 705 (1912); **19,** 480 (1913).

[2] *Ber. Deut. chem. Gesell*, **19,** 1317 (1886); **20,** 745 (1887), see further EGGERT, J., *Z. Elektrochem.*, **23,** 8 (1917); **27,** 455 (1921).

The liberation of iodine should begin immediately after the starting of the reaction and gradually increase further. But, actually, one first observes a period of time during which no iodine is liberated, after the mixing of the initial substances. Iodine appears very suddenly after some time. This astonishing behavior is best explained by the following assumptions: The actual course of the reaction does not occur according to the above gross reaction, but can be resolved into the following stages.

$$3H_2SO_3 + HIO_3 \rightarrow 3H_2SO_4 + HI \quad \text{slow} \quad (I)$$
$$5HI + HIO_3 \rightarrow 3H_2O + 3I_2 \quad \text{faster} \quad (II)$$
$$H_2SO_3 + I_2 + H_2O \rightarrow H_2SO_4 + 2HI \quad \text{rapid.} \quad (III)$$

Hydrogen iodide is first slowly formed according to (I), which is oxidized to iodine by the excess of iodate with a somewhat greater but still finite velocity. But the liberated iodine reacts practically instantaneously with the sulfurous acid and is again reduced to hydrogen iodide (Eq. (III)). Therefore, iodine can first be liberated in noticeable quantities if the sulfurous acid is used up and thus if the recurrent reaction (III) no longer comes into play. The more hydrogen iodide there is the faster reaction (II) proceeds at first and, therefore, the faster the total reaction comes to an end owing to the rapid course of (III). But now reaction (III) produces HI and, accordingly, the reaction accelerates itself in its course (auto catalysis). If one adds some HI to the initial mixture, then the reaction is highly accelerated from the start. The hydrogen iodide acts as a positive catalyst. It should be observed that this does not appear in the original gross equation for the reaction.

We see immediately that the slowest partial reaction determines the velocity of the entire process.

The oxidation of sulfurous acid to SO_3 or H_2SO_4 in the lead-chamber process represents an especially simple and sufficiently clear example of positive catalytic action, which proceeds only by means of NO or NO_2 as catalyst and in the following stages:

$$SO_2 + NO_2 + H_2O = H_2SO_4 + NO \quad (I)$$
$$NO + \tfrac{1}{2}O_2 \rightleftharpoons NO_2 \quad (II)$$

while in the gross reaction

$$SO_2 + \tfrac{1}{2}O_2 + H_2O = H_2SO_4$$

the catalyst does not appear.

As yet no final decision has been reached in regard to an explanation of the catalytic action of water vapor upon the burning of carbon monoxide. Two possibilities exist. Either it first represents the water-gas equilibrium and the hydrogen appearing thereby is again oxidized to water

$$CO + H_2O \rightarrow CO_2 + H_2$$
$$2H_2 + O_2 \rightarrow 2H_2O,$$

or it forms hydrogen peroxide as an intermediate which is doubtless more stable at higher temperatures than at lower.

$$2H_2O + O_2 = 2H_2O_2$$
$$H_2O_2 + CO = CO_2 + H_2O.$$

In numerous other cases, as, for example, in the catalysis of cane sugar inversion by H^+ ion, it has not yet been possible to clear up satisfactorily the true reaction mechanism and the intervention of the catalyst, though an interpretation through rapid intermediate reactions is also probable here.

Also the action of negative catalysts[1] may be explained for the most part by the theory of intermediate reactions and, indeed, in the way in which the negative catalyst concerned reduces the concentrations of the products which are necessary for the course of the determinative intermediate reaction. For example, Hg^{++} ions act as strong inhibitors on the course of the Landolt reaction. The most probable reason is that the concentration of the I^- ions which are indispensable for the progress of the reaction are reduced by complex formation with the Hg^{++} ions.

Not infrequently, homogeneous reactions proceed so slowly in their own phase that even a roundabout way on the boundary surface of another phase leads to an end product more rapidly than does the direct conversion within the homogeneous phase. For example, the velocity of union of oxyhydrogen gas is practically zero at ordinary temperatures without a catalyst On the other hand, a lively reaction takes place on the interface when oxyhydrogen gas is brought in contact with finely divided platinum. The platinum and its surroundings are heated so high by the heat liberated in the reaction that the reaction also assumes a finite velocity in the gas space and propagates itself there. The fact previously mentioned in **197** that hydrogen and probably oxygen are dissolved in the monatomic state in platinum is the reason why the reaction proceeds so much more rapidly on platinum than in the gas space, for it is clear that a formation of water from hydrogen and oxygen atoms must take place much more easily than from the molecules existing exclusively at lower temperatures in the gas. However, recent investigations of Langmuir[1] show that the reason for the acceleration in the reaction consists in a special activation of the oxygen molecules on the platinum surface (see **172**).

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[1] * See TAYLOR, H. S., *J. Phys Chem*, **27**, 322, 1923, CHRISTIANSEN, J. A., *ibid.*, **28**, 145 (1924) for more details.

239. Ostwald's Rule of Successive Reactions.—It may be assumed that a direct (gross) reaction leading from a number of initial substances to any stable final products proceeds with almost infinite slowness, so that the reaction must take place by the roundabout way of intermediate products if a reaction is to occur at all. Now if at the same time the velocity of some of the intermediate reactions is relatively slow, the reaction will remain for a greater or less time in one of the labile stages. This phenomenon is so frequent that Ostwald could represent it as a general rule, the so-called **rule of successive reactions.**

If the intermediate reaction also proceeded with extraordinary slowness, just as did the gross reaction, then the stable end products could not be reached within a finite time, and the reaction comes to a stop, yielding a labile intermediate product. Numerous reactions, particularly of organic chemistry, serve as examples for the latter cases. For example, the stable end product of the oxidation of methane under all conditions is water and carbonic acid, though an entire series of oxidation products lying between (alcohols, aldehydes, and acids) may be realized, according to the conditions of the experiment, which also exist for some time in contact with oxygen at ordinary temperature.

b. Heterogeneous Systems

α. CHEMICAL REACTIONS

240. General.—The initial substances in a heterogeneous system exist, originally at least, in part in different phases. The rapidity of the exchange therefore depends upon:

1. How rapidly the substances reach the different phases where the reaction really takes place.

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[1] *Trans. Faraday Soc*, **17**, 607, 621 (1922).

2. With what velocity the true chemical reaction proceeds in the place of reaction.

3. How rapidly the reaction products formed are transported away from the place of reaction.

The influences mentioned under (1) and (3) are, in principle, of the same type and, therefore, may be classed together in what follows. The speed of a heterogeneous reaction is determined by that phenomenon which proceeds most slowly, just as the slowest intermediate reaction determines the entire conversion in a homogeneous reaction occurring in different steps. Therefore, according to whether the velocity of transport exceeds the chemical-reaction velocity or *vice versa* two theoretically different phenomena are found.

For a chemical-reaction velocity which is relatively slow in comparison to the transport velocity, the substances always have sufficient time to equalize their concentrations within a single phase. The reaction then proceeds, as a rule, in *one* definite reaction phase (the gas or a liquid phase), according to laws valid for homogeneous systems. It is very infrequent that a reaction occurs at the same time in several phases.

With greater chemical-reaction velocities the concentrations within the given phases and especially in the reaction phase itself, are no longer completely equalized. Let us consider the reaction of a gas with a solution such as the union of oxygen with pyrogallol dissolved in water as an example On the surface the liquid will be saturated with oxygen and, on the contrary, be relatively poor in pyrogallol. But relatively little oxygen reaches the interior, since it will be used up on its way there, and, on the contrary, the pyrogallol concentration remains relatively high. The slower the oxygen and pyrogallol molecules migrate forward and the greater the chemical reaction velocity the smaller will be the range within which the chemical reaction proceeds. A conversion will only occur in a thin layer in the immediate neighborhood of the interface of the two phases for reactions proceeding rapidly. If the reaction proceeds very briskly, this reaction layer is confined to a thickness of molecular dimensions. Instead of calculating such cases as homogeneous reactions, it appears expedient to look upon them as a special type of reaction and to designate them as *surface reactions.* It is probable that such reactions occur considerably more frequently than was previously believed.

In addition to the true surface reactions, it is also necessary to take account of those numerous reactions in which an adsorbed gas covering the surface with only a single layer of molecules (see **172**) reacts with another gas in which the surface of a foreign phase acts catalytically by the activation of the molecules absorbed by it.

241. The Predominant Influence of Diffusion Velocity. In numerous heterogeneous reactions, the chemical-reaction velocity (homogeneous or surface) may be regarded as relatively large compared to the transport velocity. The quantity transformed depends exclusively upon the velocity with which the materials taking part in the reaction reach one another.

A diffusion process alone can effect the transport of a reactant in a system which is homogeneous and is not subjected to any mechanical influences, and owing to the minuteness of the diffusion coefficients, especially in solution, this generally proceeds quite slowly. In case motion is produced in a single phase by mechanical devices (stirring) or temperature differences (convection), the concentration differences formed by the reaction will be very rapidly equalized. By this means the transport of the reactants, and therefore the chemical conversion, will be powerfully increased. But, in spite of the most brisk stirring, an adhering layer will exist at the interface between the two phases, which does not move with the bulk of the solution, and which can only be penetrated by the aid of diffusion, so that, *in the last analysis, diffusion determines the velocity of the chemical change* (Nernst).

The dissolution of magnesia in an acid, investigated by Brunner,[1] may now be considered as an example of a heterogeneous reaction in which the true chemical reaction proceeds very rapidly, and the entire course of the reaction depends only upon the transport of the reacting substances by diffusion.

$$MgO + 2HCl \rightleftharpoons MgCl_2 + H_2O.$$

The experiment may be carried out by putting a piece of magnesia of definite surface in an acid solution which is stirred violently. The progress of the reaction can be measured in different ways, such as weight of the magnesia, concentration of the acid, etc.

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[1] *Z. physik Chem*, **47**, 56 (1904).

As a result of the stirring, the concentration of the acid within the solution may be regarded as constant c. On the contrary, in the immediate neighborhood of the magnesia surface the acid is immediately used up and its concentration, therefore, remains very small (c_0). Now the quantity of acid dn reaching the solid magnesia, upon the amount of which the magnitude of the chemical change depends, may be calculated from Fick's first law (Eq. (351))

$$dn = Dq\frac{c - c_0}{\delta'}dt, \tag{247}$$

where δ' indicates the thickness of the adhering layer through which the diffusion occurs and the quotient $\frac{c - c_0}{\delta'}$ is substituted for $\frac{dc}{dx}$.

Therefore, the decrease in concentration of the hydrochloric acid in a unit of time amounts to $\frac{dn}{vdt} = -\frac{dc}{dt}$. Now it is assumed that c_0 is small compared to c, so that, finally,

$$\frac{-dc}{dt} = \frac{Dq}{v\delta'}c \tag{247a}$$

This equation agrees in form with the differential Eq. (240) valid for a homogeneous unimolecular reaction, if we set $k = \frac{Dq}{v\delta'}$.

Equation (247) has been confirmed by experiment for numerous heterogeneous reactions, and especially for the solution of salts in water.[1] In the latter cases a saturated solution always exists directly upon the crystal surface and the salt diffuses from here through the adhering layer into the unsaturated solution.

Sometimes, however, Eq. (247) does not prove to be directly applicable, as, for example, in the crystallization of some salts from their supersaturated solution,[2] an evidence that the diffusion velocity does not alone determine the course of the total process but that a further time-consuming intermediate process is to be borne in mind, which, obviously, concerns the arrangement of the molecules in the space lattice during the crystallization.

Frequently, secondary influences exercise a powerful effect upon the course of heterogeneous reactions. For example, the oxidation of yellow phosphorus by gaseous oxygen comes to a standstill if its partial pressure exceeds a value of 730 *mm* at 18°C. It is possible to assume that the obstruction of the reaction consists in a layer of the final, or perhaps also of an intermediate, reaction product which is impermeable to oxygen, and whose formation is favored by a higher partial pressure of oxygen.[3]

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[1] NOYES and WHITNEY, *Z. physik. Chem.*, **23**, 689 (1897).

[2] MARC, *Z. physik. Chem.*, **79**, 71 (1912).

[3] * However, JORISSEN, W. P. (*Rec. trav. chim. Pays-Bas*, **40**, (4th series), 539 (1921)) considers that it is due, instead, to the fact that no combustion of phosphorus vapor occurs when the ratio of the concentration of oxygen to phosphorus vapor exceeds a critical value corresponding to the lower limit of explosion in the gas phase.

The temperature coefficient of those heterogeneous reactions whose velocities are conditioned by diffusion effects must obviously be the same as the diffusion coefficient. Since the latter increase on the average only about 2 to 3 per cent per degree, they are considerably less influenced by temperature than are most homogeneous reactions.

β. ELECTROCHEMICAL REACTIONS

242. Primary and Secondary Electrochemical Reactions.—Electrochemical reactions, *i e*, such reactions as take place on the conduction of current through an electrolyte (electrolysis) on or in the immediate neighborhood of the electrodes, form a special class of heterogeneous reactions

Here also the total quantity converted depends, as above:

1. Upon the velocity of transportation of the reacting participants, and
2. Upon the velocity of the chemical change.

The true reactions taking place in an electrolysis consist, as a rule, of a primary and a secondary process. The primary reaction consists in an electrical charging of the atoms or radicals or in a discharge or recharging of the ions. The secondary process consists in an exchange between the primary products themselves—say, following an association--with the electrodes, or with a substance existing in the electrolyte.

While the reaction velocity of the primary electrochemical process probably is always extraordinarily great,[1] the secondary reactions, as a rule, possess the characteristics of ordinary chemical reactions, and proceed with varying velocities.

In what follows only those electrochemical processes in which only primary reactions and rapid secondary reactions take place will be exhaustively discussed. The electrochemical exchange depends upon the rapidity with which the ions are brought to the electrode from the solution, just as in the heterogeneous reactions considered in **241**, or, in case soluble reaction products (ions) are formed in the reaction, with the rapidity with which the latter are removed from the electrodes.

If a slow reaction is connected with the primary reaction, then the total exchange will depend not alone upon the transport of the ions but also upon the velocity of the secondary reaction. In general, the laws of homogeneous reactions hold for the course of the latter only when the concentrations are not uniform throughout, just as in the example in **241.** Regarding an electrolysis, the course of which is determined by a secondary reaction (the saponification of ester by OH^- ions), and which has been quantitatively worked out, (see EUCKEN, A., *Z. physik Chem*, **71**, 550 (1910)) Haber and Russ treat the limiting case of a very slow chemical reaction (*ibid*, **47**, 257 (1904)).

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[1] Eucken, *Z. physik. Chem.*, **64**, 562 (1908).

243. Direct Ionic Transport by the Current.—The transport of ions from the solution to the electrode generally takes place in different ways, according as the current acts for a short or longer time. It will be assumed that the two electrodes in the solution are of the same nature throughout at the start. If a direct current[1] is permitted to flow through for only a very short time it will produce no marked changes. The only force acting upon the ions, then, is the electrical field, which is due to the potential applied to the electrodes from the outside. As already derived above in **183**, one obtains for the conductivity κ of the solution under this assumption,

$$\kappa = \Lambda c = \alpha\mathfrak{F}(U^+ + U^-)c. \qquad (190)^2$$

upon which the strength of the current for a given potential and, therefore, the magnitude of the electrochemical conversion directly depends.

Now the quantities u^+ and u^-, which are designated as the mobility of the corresponding ions, are frequently substituted for $\alpha\mathfrak{F}U^+$ or $\alpha\mathfrak{F}U^-$. Although for weak electrolytes the migration velocities U^+ and U^- are considered constant, and α has been regarded as changing with concentration, it is more correct for strong electrolytes (*cf.* **188**) to consider α as a constant equal to unity and U or u as variables. Now for a large number of strong electrolytes—for example, for all binary salts of the type NaCl—the individual values of U and, therefore, also of u, show nearly the same change with concentration in every combination. The empirical formula for α'' may be directly applied to u, in which $\alpha'' = \frac{U_v}{U_\infty}$ is substituted analogous to (Eq. (191)).

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[1] Symmetrical alternating currents call forth no changes in the electrolytes with experiments of long duration, because the action of every current force directed toward the left is annulled by the current force directed toward the right following upon it.

[2] In this formula the concentration c expresses gram equivalents per liter instead of the usual moles per liter.

Therefore, in these cases Λ_c can be calculated from the equation: $\Lambda_c = U^+ + U^-$, by using the definite values of u given for a number of ions in Table 62.

TABLE 62

Ion	Mobility u at 18°C				Temperature coefficient in per cent $\left(100 \frac{1}{u_{18}} \frac{du}{dT}\right)$
	$c = 0$	$c = 0.001$	$c = 0.01$	$c = 0.1$	
H^+	0.3145	0.3118	0.3070	0.2944	1.54
Li^+	0.0333	0.0313	0.0301	0.0258	2.65
Na^+	0.0435	0.0423	0.0400	0.0354	2.44
K^+	0.0645	0.0631	0.0604	0.0554	2.17
Cs^+	0.068	0.066	0.0635	0.0580	2.12
Ag^+	0.0543	0.0526	0.0500	0.0449	2.29
$\frac{1}{2}Zn^{++}$	0.046	0.0420	0.035	0.024	2.54
$\frac{1}{2}Mg^{++}$	0.046	0.042	0.036	0.026	2.54
OH^-	0.174	0.171	0.167	0.157	1.80
F^-	0.0466	0.0430	0.0403	0.036	2.38
Cl^-	0.0655	0.0642	0.0620	0.0566	2.16
Br^-	0.0670	0.0657	0.0634	0.0579	2.15
I^-	0.0665	0.0652	0.0629	0.0574	2.13
NO_3^-	0.0618	0.0605	0.0578	0.0494	2.05
$CH_3CO_2^-$	0.0350	0.0323	0.0306	0.0262	2.1
$\frac{1}{2}SO_4^{--}$	0.0683	0.064	0.056	0.040	2.3

Also, salts which are composed of uni- and bivalent ions are adapted for the greater part to this scheme (exception: H_2SO_4), though other numbers are required for the calculation of the molecular conductivity of salts which are composed of two bivalent ions, for example, $ZnSO_4$.

If we confine ourselves to a fixed group of strong electrolytes in which u shows about the same dependence on the concentration, the Kohlrausch law (see **182**) holds not only for infinite but also for finite dilutions (see footnote, page 304).

244. Migration and Ionic Radius (Hydration).—According to (Eq. (186)), U, and therefore u also, are inversely proportional to the frictional force f. If the ions are represented as small spheres suspended in water, which, of course, is only a rough approximation, then f has the value $6\pi a\eta$ according to Stokes, where a represents the radius of the sphere and η the frictional coefficient of the solvent. Therefore,

$$u \sim \frac{1}{a\eta}. \tag{248}$$

In the same solvent (η = constant) u should be inversely proportional to the ionic radius. On comparing this requirement with the data in Table 62, it appears that the Li^+ ion must possess a greater diameter than the Na^+ ion and the latter a greater one than the K^+ ion etc., while the atomic diameters are doubtless in the inverse order. The best explanation of this striking phenomenon consists in the assumption of hydration, i.e., there are a number of ions, particularly the Li^+ ion and the F^- ion, which are conceived as surrounded by an envelope of water. As M. Born[1] has shown convincingly, it is not necessary to seek the reason for this hydration in chemical forces, but, instead, the hydration is represented as a simple electrostatic effect. The neutral water molecules are drawn to the ions similarly to an electrically neutral shred of paper by an electrified rod of hard rubber. The smaller the size of the true ion the more the lines of force radiating from it are crowded together, and the greater is their effect upon the molecules of the solvent, thus a number of water molecules will be more powerfully retained by the ion of smaller diameter.

It is clear that the true ionic radius of the small Li^+ and F^- ions will be powerfully increased by hydration, while the hydration will be less for the ions whose true radius is larger.[2] The complete calculation leads to the noteworthy result that the true ionic radius of the positively charged alkali metals (without the envelope of water) is considerably smaller than that of the neutral atoms, which agrees excellently with the conceptions developed in Sec. D.[3]

Now according to Born's theory the H^+ ion, on account of its small size, is especially heavily hydrated, which does not at first appear to be in agreement with its strikingly high mobility. However, it is to be assumed that the H^+ ion does not migrate back and forth through the water unchanged as the other ions, but, instead, it is very frequently swallowed up by the water molecules on the one side and given up again by the others (the same holds true for OH^- ions), so that these ions avoid a large part of the path involving friction.

That the transport of current by the H^+ and OH^- ions in water is really of different nature than that of the other ions is also shown by the abnormal temperature coefficient of their mobility (see **243**).

245. Ionic Mobility and the Viscosity of the Solvent.—If a larger ion whose hydration is small is considered—for example, Cs^+ ion—and, therefore, whose effective ionic radius is practically identical with the true ionic radius, then, according to (Eq. (248)), it would be expected: (1) that the temperature coefficient of mobility varies inversely as the frictional coefficient of the solvent, (2) that the mobility in different solvents is inversely proportional to the coefficient of friction Both conclusions are well established. The temperature coefficient of mobility of heavy ions amounts to 2.3 to 2.5 per cent per degree at room temperature, while the viscosity of water changes 2.43 per cent per degree. This agreement exists also at higher temperatures up to 150°.

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[1] *Z. Elektrochem.*, **26**, 401; *Z. Physik*, **1**, 221 (1920). * See also the papers by DEBYE and HÜCKEL, *Physik. Zeit.*, **24**, 305 (1923) and later papers by HÜCKEL in the same journal (*cf.* **191a**).

[2] See also **349** and **350**.

[3] * See SCHMICK, H., *Z. Physik.*, **24**, 56 (1924).

Walden investigated the mobility of certain ions in different solvents[1] and found that the above requirements were usually well satisfied. The limiting molecular conductivity of certain salts in different solvents may be represented with satisfactory accuracy by $\Lambda_\infty = U^+_\infty + U^-_\infty = \frac{Const.}{\eta}$ even when Λ_∞ and η vary within wide limits It is remarkable that water alone does not conform to this rule, at least for electrolytes of small (inorganic) ions. This fact has not as yet been completely accounted for theoretically.

246. Hittorf Transference Numbers.

246. Hittorf Transference Numbers.—Owing to the effect of the potential, the anions migrate to the anode and the cations to the cathode and concentration differences appear in the electrolyte with experiments of long duration. As an example, first consider the electrolysis of silver nitrate between silver electrodes, in which silver dissolves at the anode and an equal quantity is precipitated on the cathode The transport of current in the solution results not alone from the silver ions but also from the oppositely charged and therefore oppositely migrating NO_3^- ions.

While a definite quantity of silver, say, one gram-atom, corresponding to $1\mathfrak{F}$ of electricity, is dissolved at the anode, only a part of the ions formed migrate away to the cathode, but, on the contrary, a quantity of NO_3^- ions equivalent to the residue remaining behind migrates to the anode. Therefore, an increase occurs at the anode and, correspondingly, a decrease in $[AgNO_3]$ at the cathode, since more silver ions are deposited here than migrate towards it. As Fig. 55 shows, the concentration changes in the preceding example are greater the faster the anion migrates in comparison to the cation. The quantitative connection between the changes of salt concentration at the electrodes and the ionic mobilities results from the following consideration.

The total quantity of current passing through the electrolyte is given by Eq. (187). It dissolves at the anode in unit time;

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[1] Latest publications *Z anorg. Chem.*, **113**, 118 (1920).

the quantity of silver $n = (U^+ + U^-)c_iq\frac{\Delta E}{l}$. Now $\Delta n' = U^+c_iq\frac{\Delta E}{l}$ silver ions migrate away, while $\Delta n = U^-c_iq\frac{\Delta E}{l}$ nitrate ions migrate towards the anode.

The increase in the quantity of silver ions at the anode amounts, therefore, to:

$$n - \Delta n' = (U^+ + U^- - U^+)c_iq\frac{\Delta E}{l} = U^-c_iq\frac{\Delta E}{l} = \Delta n$$

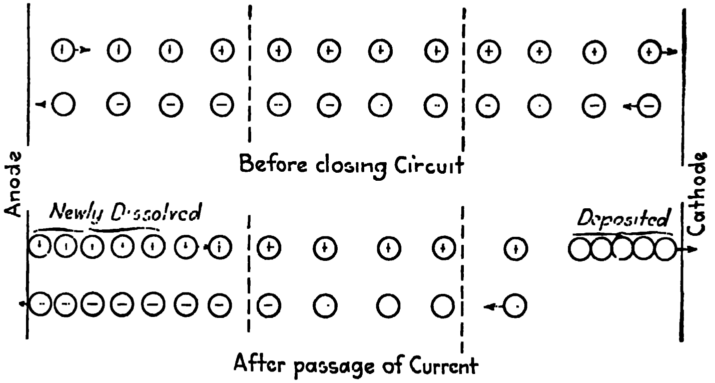

FIG 55

and is, in fact, equal to the increase of NO_3^- ions and hence total $AgNO_3$. From this it follows directly that

$$\frac{U^-}{U^+ + U^-} = \frac{u^-}{u^+ + u^-} = \frac{\Delta n}{n} = n_a,$$ and, analogously,

$$\frac{u^+}{u^+ + u^-} = \frac{\Delta n'}{n} = n_k. \qquad (249)$$

The ratios n_a or n_k are designated as the **Hittorf transference numbers** of the anion or of the cation. These numbers can be determined experimentally by analysis and by the use of a silver coulometer, and in conjunction with the sum $u^+ + u^-$ obtained from conductivity measurements they permit of a calculation of the individual values of u^+ and u^-.

The sum of the transference numbers of the anion and cation $n_a + n_k$, has, according to (Eq. (249)), the value 1. Since the mobilities represent positive quantities, the transference numbers must always lie between 0 and 1.

Now complex ions (**192**)—for example, the $Ag(CN)_2^-$ ion, in which the metal is preponderantly combined as anion—migrate against the current. Since in this case there is no migration away from, but, instead, a migration of silver containing ions occurs toward the anode, Δn is greater than n and, therefore, a value is found which is greater than unity for the apparent transference number of the anion and a negative value for the transference number of the cation n_k in case Eq. (249) is applied schematically to $KAg(CN)_2$ just as to $AgNO_3$. From this state of affairs, Hittorf first derived the important result that the silver in $KAg(CN)_2$ does not migrate as cation as with $AgNO_3$, but is united to an anion just as are the metals in numerous other complex salts.

The actual transference number of $KAg(CN)_2$ in the calculation of which the combination of silver as anion is borne in mind, obviously, lies between 0 and 1, corresponding to the requirement above.

247. The Electrolysis of Alkali Salts.—While concentration displacements occur only in the electrolysis of a metallic salt in the neighborhood of the electrodes of the corresponding metal, yet in other cases more fundamental changes occur For example, if a NaCl solution is electrolyzed between unattackable electrodes, such as platinum, then the Na^+ ions migrate to the cathode and the Cl^- ions to the anode. While the latter may be liberated as a gas, hydrogen appears at the cathode instead of metallic sodium, since the deposition of the latter requires considerably less expenditure of work than does that of sodium (see Table 46)

While the solution becomes deprived of sodium ion as well as chloride ions at the anode, the sodium ions accumulate about the cathode. At the same time OH^- ions remain behind, owing to the deposition of H^+ ions, *i. e.*, the solution becomes alkaline.

This reaction forms the foundation of various important technical processes for the electrolytic extraction of alkali on the one side and of chlorine from the alkali chlorides on the other side.

It requires a smaller expenditure of work to decompose the water than to deposit the anions of the salts in the electrolysis of dissolved alkali sulfates, nitrates, and some other salt solutions.

In such cases oxygen is produced at the anode, so that the solution loses OH^- ions and therefore becomes acid.

248. Galvanic Polarization.[1]—Now the changes called forth by the passage of current through the electrolyte and at the electrodes have shown that new forces acting on the ions, other than the original drop in potential, appear, so that the transfer of ions undergoes a complete change from that of the initial state. First, the resulting concentration changes are synonymous with the appearance of an osmotic-pressure difference, which acts directly upon the ions as a driving force. Further, changes called forth as a result of the electrolysis occur in the solution, especially electromotive forces at the electrodes which are directed against the potential imposed This phenomenon, especially important for electrolysis and discussed more fully in what follows, is called "galvanic polarization" The difference between the imposed potential and the polarization determines the electrical field actually acting upon the ions.

249. Stationary State during the Passage of Current through an Electrolyte.—The changes which the electrolyte and the electrodes suffer on electrolysis of long duration do not, as a rule, increase continuously, but, instead, tend to reach a definite limiting value. When a definite potential is put across an electrolytic trough, after some time a "stationary state" is reached in which the quantities characteristic for the reactions, concentrations, nature of the electrodes, polarization, and current strength temporarily assume constant values. If the potential is changed, then the corresponding stationary state is destroyed, and some time is required before the system has adjusted itself to the new conditions, and polarization, current strength, etc. have again become constant. In the following, considerations important for the stationary state will be discussed in contrast to those (**243**) valid only for the non-stationary initial state. In case the solution electrolyzed is not free from convection currents and the like, or if the solution is intentionally subjected to stirring, no concentration changes can be produced in the interior of the solution and the appearance of a stationary state is confined then to the electrodes and the liquid layer adhering directly to the electrodes as mentioned in (**241**).

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[1] Summarized report, KRUGER, F, *Z. Electrochem.*, **16**, 522 (1910).

* See also ALLMAND, "Principles of Applied Electrochemistry," Arnold (1920).

250. Deposition Polarization (Decomposition Potentials).[1]—In some cases the limiting value of the polarization is very nearly equal to the polarizing potential. The electrolysis, say, of normal hydrochloric acid, between a large hydrogen electrode as cathode and a small platinum electrode as anode at a low potential serves as an example of this.[2]

A small current passes through the solution the first moment after applying the potential. A small quantity of chlorine is deposited by it on the anode with which the platinum becomes charged. The platinum anode in this way becomes a chlorine electrode and therefore exercises an *e m f.* opposite to the original potential against the hydrogen electrode. A polarization results, owing to the deposition of chlorine, which may suitably be designated as **deposition polarization.** The higher the platinum electrode is charged with chlorine the more the polarization increases, and the original current strength falls correspondingly. Finally, as soon as the polarization has reached a value approximating the value of the imposed potential, no more current goes through the solution. The partial pressure of chlorine with which the platinum electrode is charged at low potentials is extremely small and still lies far under atmospheric pressure at about 1 *volt*, so that the chlorine may escape as a gas. The potential of a chlorine-hydrogen gas cell (see **217**) under atmospheric pressure is first reached at a potential of 1.36 *volts*. The chlorine now assumes a partial pressure of 1 *atm.* and can escape as a gas. From this point on the partial pressure of Cl_2, and therefore the polarization, cannot increase further, even if the potential is increased. The current strength which previously was practically zero increases greatly from the point 1.36 *volts*, which is the decomposition potential of HCl

Owing to deposition polarization, one may easily separate metals, such as zinc and copper, whose potentials are widely different from one another, by electrolysis. Practically, only the nobler metal (Cu) is deposited from a solution containing both ions at small potentials ($<$ about 0.6 *volts* against the H_2 electrode), since an exceedingly small quantity of zinc, not detectable analytically, suffices to call forth a polarization which is very nearly equal to the imposed potential.[1] Accordingly, the potential must in all cases be higher than 0.8 *volt* (measured against the H_2 electrode) to deposit pure zinc after the exhaustion of the copper ions or zinc and copper simultaneously in the presence of copper ions.

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[1] The phenomena described in this paragraph were first clearly recognized and correctly explained by Le Blanc (1891).

[2] If a large electrode is inserted against a small one, then it is necessary only to consider the changes at and in the neighborhood of the small electrode.

251. Concentration Polarization (Diffusion Currents).—Another typical case is met in the electrolysis of a potassium iodide solution containing a little iodine. A small platinum point and a large platinum sheet serve as cathode and anode. The surface of the latter is so great that its changes and also the concentration changes in its neighborhood are relatively small and it can, therefore, be designated as non-polarizable. Both electrodes become charged with iodine and act approximately as reversible iodine electrodes.

Now if a relatively small potential of a few tenths of a volt is applied to the electrodes, then the iodine will be reduced to iodide ions while the potassium and hydrogen ions of the water cannot become discharged owing to the small potential. According to Table 46 it requires a potential of at least 0 54 *volt* apart from the influence of ion concentrations in order to deposit hydrogen cathodically against an iodine electrode as anode, while almost any small potential suffices for the cathodic reduction of elementary iodine. Now an impoverishment of iodine occurs in the immediate neighborhood of the cathode during the passage of current, while in the solution and on the surface of the anode its concentration remains practically constant. According to Henry's law, a different partial pressure of iodine prevails at the two electrodes and we are therefore concerned with a gas cell of the type discussed in **217.** The *e.m f.* of this cell in a direction opposite the original potential depends upon differences of concentration or of partial pressures of a substance and therefore is designated as concentration polarization. Now this potential increases with the impoverishment of the iodine molecules at the cathode. Finally, in the stationary state it becomes as great as the polarizing potential E, though, obviously, it can never exceed this value. Therefore, for the limiting value of the polarization E_p on the basis of (Eq. (221)):[1]

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[1] That copper deposits, in spite of this, is brought about by the phenomenon of diffusion currents. This is discussed in the following paragraph.

$$E = E_p = \frac{RT}{2} \ln \frac{c_0}{c_k}, \tag{250}$$

where c_0 represents the concentration of I_2 in the solution or at the anode and c_k that at the cathode.

Now iodine reaches the cathode entirely by diffusion from the solution. The quantity of iodine $\frac{dn}{dt}$ reaching there in a unit of time is determined by Fick's first law, in which $\frac{c_0 - c_p}{\delta'}$ (δ' is the thickness of the diffusion layer) is set in place of the differential quotient $\frac{dc}{dx}$, just as in **241.**[2] So long as the discharge of iodine is the only possible electrochemical reaction, the current flowing through the electrolyte equals the quantity of electricity ($2\mathfrak{F}$ per mole I_2) in the time dz for the quantity of iodine dn transported, *i.e.*,

$$I = 2\mathfrak{F}\frac{dn}{dt} = \frac{2\mathfrak{F}Dq(c_0 - c_k)}{\delta'}, \tag{251}$$

where q represents the cross-section of the diffusion layer or, what usually amounts to the same thing, the surface of the small cathode.

Eliminating c_k from Eqs (250) and (251), a relation between I and E, the so-called current potential curve of the process, is obtained in which all quantities can be determined physically. When E is chosen as abscissa and I as ordinate, the current-potential curve first rises rapidly, but soon becomes parallel to the abscissa axis at about a potential of 0.1 *volt*, *i.e.*, the current I is independent of the potential. This effect is easily understood if it is considered that, for sufficiently high values of E or E_p, c_k must become extremely small compared to c_0, so that c_k disappears in Eq. (251) and therefore only constant quantities remain on the right side. The horizontal branch of the current-potential curve is called the "limiting current," while the entire phenomenon is called a diffusion current, since the current strength depends only upon the diffusion velocity of I_2. The current strength exceeds the value of the limiting current at higher potentials when new electrochemical reactions become noticeable (discharge of H^+ ions) (see Fig. 56).

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[1] Using concentrations in place of activities

[2] Until the stationary state has set in, the differential Eq. (36) holds for the diffusion reaction. But since in the stationary state no true changes occur, we obtain here $\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2}\right) = 0$. From this it follows that $\frac{\partial c}{\partial x} =$ *Const.* The drop in concentration in the diffusion layer is, therefore, equally great throughout and $\frac{c_0 - c_p}{\delta'}$ can be substituted for it.

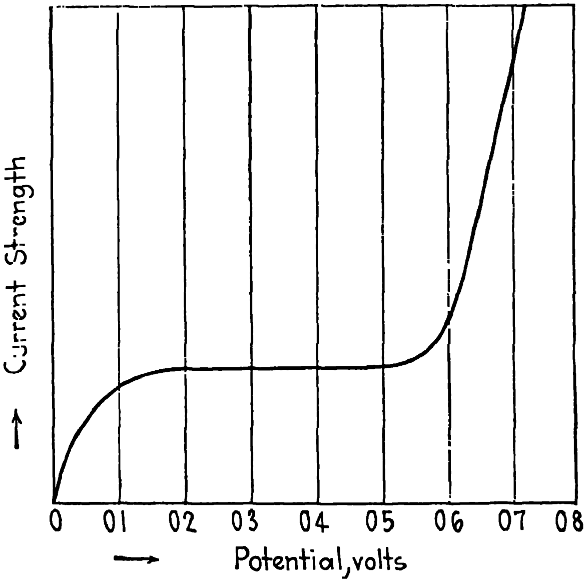

FIG 56

While, therefore, Ohm's law holds for metallic conductors and non-stationary electrolytic processes in which no polarization can be built up (electrolysis of short duration or weak alternating current), according to which the potential is simply proportional to I, the current-potential curve of an electrolyte in the stationary state shows an entirely different course, particularly at low potentials.

A further typical example of the appearance of concentration polarization is the electrolysis of a metallic salt ($AgNO_3$) between two electrodes of the same metal (Ag). In case the stationary state is actually reached the silver ions migrate in a stream through the solution, while the NO_3^- ions cannot take part in the conduction of current at all, since they cannot be produced or used up by the electrolysis at any place. The total force acting upon them must, therefore, equal zero. This is due to the fact that the electric force acting upon the NO_3^- ions compensates the osmotic-pressure difference corresponding to the fall in concentration produced. Now with the Ag^+ ions the sign of the electric force is reversed, and therefore the osmotic-pressure difference and the electrical force operate in the same direction, *i.e*, the osmotic-pressure difference acting upon the cation is doubled by the electric force. The current strength is likewise represented by Eq (251) (diffusion current), except that the factor 2 enters, owing to the doubling of the osmotic force. Moreover, in this case, the course of the current-potential curve is, theoretically, the same as with a pure diffusion current. The polarization called forth by the difference in concentration of the Ag^+ ions can be calculated by Eq (250). In this case it is half as great as the applied potential. (For further details see EUCKEN, A., *Z. physik. Chem.*, **59**, 72 (1907).)

In the electrolysis of Na_2SO_4 and similar salts, alkaline reactions appearing at the cathode and acid reactions appearing at the anode produce a polarization, which corresponds to the potential of the acid-alkali cell (acid-alkali polarization), and likewise represents a type of concentration polarization For the steady state, the transport of current is effected by H^+ ions at the anode migrating to the interior of the solution, and at the cathode by the OH^- ions. A neutral layer exists in the middle The Na^+ and $SO_4^=$ ions cannot participate in the conduction of current in the steady state, since they are neither produced nor used up. The drop in concentration of the Na^+ and $SO_4^=$ ions is opposite in direction.

In addition to the acid-alkali polarization a deposition polarization also appears on the electrolysis of Na_2SO_4, since different gases (H_2 and O_2) are developed at both electrodes. The cathode therefore behaves as an H_2 electrode and the anode as an O_2 electrode.

252. Chemical Polarization Accumulators.—"Chemical polarization" is closely related to deposition polarization. For example, if sulfuric acid saturated with lead sulfate is electrolyzed between two lead electrodes, then the Pb^{++} ions become oxidized to lead peroxide at the anode, lead is deposited at the cathode, and a polarization is produced corresponding to the *e.m f.* of the cell.

$$\mathrm{PbO_2} \left| \begin{array}{c} \mathrm{H_2SO_4} \\ \text{saturated with} \\ \mathrm{PbSO_4} \end{array} \right| \mathrm{Pb}.$$

The production of PbO_2 and Pb on the anode and cathode respectively continues for a still longer time at a potential which suffices for the maintenance of a current even after the formation of this polarization.

If the polarizing current is interrupted, a galvanic cell results, which on its own account is able to deliver a current until the PbO_2 and Pb formed are used up. Such a cell is adapted for the storage of electrical energy and is called an accumulator.

The greater the quantity of PbO_2 or Pb formed the more current the accumulator can yield and, therefore, the greater is its capacity. However, during the discharge the *e.m f.* of the lead accumulator does not remain constant to the exhaustion of the PbO_2 and Pb, but gradually becomes smaller. This is due to the fact that its *e.m.f.* depends to a high degree upon the concentration of the sulfuric acid. High SO_4^{-} ion concentration represses the Pb^{++} concentration, and therefore makes the Pb electrode (negative pole) more negative, while at the same time a high H^+ ion concentration makes the PbO_2 electrode more positive, since the potential of a PbO_2 electrode depends upon the H^+ ion concentration similar to that of the permanganate electrode (see **218**). Since H^+ and SO_4^{-} ions are used up on discharge according to the equation

$$PbO_2 + Pb + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O,$$

the gradual decrease of the *e.m.f.* can be understood.[1]

The Edison accumulator, which is distinguished from the lead cell by its smaller weight, has found a certain field of application. It consists of the combination

$$Fe/4N\ KOH/(Ni_2O_3 \cdot 1.2H_2O).$$

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[1] Further details regarding the reactions in the lead accumulator are to be found in the monograph of Dolezalek, F., "Theorie des Bleiakkumulators," Halle (1901); and in textbooks on electrochemistry.

The current-producing process is represented by the reaction:

$$Fe + (Ni_2O_3\ 1.2H_2O) + 1.8H_2O \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftarrows}} Fe(OH)_2 + 2Ni(OH)_2.$$

Its *e.m f* amounts to about 1.34 *volts*.

253. Irreversible Polarization. Overvoltage.—The types of polarization previously pictured represent electromotive forces which correspond directly to those appearing in the galvanic cell. They can all be designated as reversible polarization phenomena. Now, in fact, in numerous cases of electrolysis an *e.m f.* appears in addition to reversible polarization, which possesses no counterpart in the *e m f.* of galvanic cells, and therefore is suitably designated as irreversible polarization. The irreversible polarization in the deposition of gases is especially striking, though it doubtless also appears in metallic deposition [1]

If a dilute H_2SO_4 solution is electrolyzed, then the process proceeding most easily at the anode is a deposition of gaseous O_2.

TABLE 63

Electrode	Overvoltage of oxygen, *volt*
Ni (spongy)	0 05
Ni (smooth)	0 12
Fe .	0 24
Pt (platinized)	0 24
Pd (smooth)	0 42
Pt (smooth)	0 44
Au	0 52

According to **214**, it is to be expected that O_2 under atmospheric pressure would be developed at a potential of 1 234 *volts*. In fact, however, a higher potential than 1.234 *volts* (measured against the normal H_2 electrode) is required, in order to allow a current to flow continuously through a H_2SO_4 solution. The total polarization is, therefore, greater than the reversible value of 1.234 *volts*. The amount of the polarization which exceeds the reversible potential is called **overvoltage.** Its magnitude, as Table 63 shows, depends to a high degree upon the electrode material.

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[1] * Various theories of overvoltage have been given by BANCROFT, *J. Phys. Chem.*, **20**, 396 (1916); MACINNES and ADLER, *J. Am. Chem. Soc.*, **41**, 194 (1919); **42**, 2233 (1920); BIRCHER and HARKINS, *ibid.*, **45**, 2890 (1923); NEWBERRY, *J. Chem. Soc*, **109**, 1051, 1359 (1916).

TABLE 64

Electrode	Overvoltage of hydrogen, *volt*
Pt	0.000
Au	0.017
Ni	0.14
Cu	0.14
Fe	0.17
Pb	0.36
Hg.	0.44

With other gases, the series of metals is entirely different. The numbers given for H_2 in Table 64 hold for the rough metal.[1] The values of the overvoltage given here are determined by the break in the current-potential curve, where the current strength increases and the development of gas bubbles begins. If the potential is raised further, then the current increases markedly, but, as a rule, the polarization also increases. This amount of overvoltage is greater the greater the current density chosen, *i.e.*, the ratio of the current strength to the electrode surface, and reaches values of about some tenths of a volt, which are to be added to the values given in the preceding tables.

Overvoltage leads to the conclusion that in electrolysis another (secondary) electrochemical progress is occurring in many cases in place of the gas development expected by consideration of the ionic concentrations (Eq. (222)).

Without overvoltage, hydrogen would be developed at the lead pole in charging the lead accumulator, owing to the magnitude of the H^+ ion concentration and the minuteness of the Pb^{++} ion concentration, and no lead would be deposited. Small traces of Pt which are brought into the accumulator in dissolved form and precipitated upon the lead plate actually reduce the overvoltage to nearly that of hydrogen. It, therefore, becomes impossible to reduce the lead sulfate, *i.e.*, the accumulator is ruined.

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[1] Taken for the most part from THIEL and BREUNING, *Z. anorg. Chem.*, **83**, 329 (1913).

The mercury process (see **247**) for the electrolytic preparation of alkali, in which the alkali metal is first taken up by a Hg cathode as amalgam, serves as a further example of the effectiveness of overvoltage The formation of the Na amalgam is possible in spite of its relatively high potential, because hydrogen cannot escape owing to its high overvoltage on mercury. In order to prepare an alkaline solution from the alkali amalgam, the latter is covered over with water and brought into contact with metallic iron. Owing to the smaller overvoltage of H_2 on iron, gaseous H_2 can form on the latter and the alkali metal goes into the solution as ion.

Overvoltage doubtless owes its origin to an obstruction which opposes the formation of gas as bubbles. Different explanations exist as regards details. Either the union of the atoms discharging as molecules of O_2 or H_2 requires a noticeable time, so that gases are crowded on or in the electrode in the monatomic state, or the atoms unite to from diatomic molecules but find no opportunity to coalesce to gas bubbles, similar to the delay in boiling.[1] Both explanations are in agreement, in that a gas is developed in the electrode in electrolysis under overvoltage, regardless of whether it is considered to be in the mon- or diatomic state, which must possess a considerably higher electromotively active "overpressure" than under reversible conditions. With this hypothesis "overpressures" can be imagined which are considerably higher than other considerations would permit. According to Eq. (225) 0.03 *volt* corresponds to a tenfold multiplication in pressure.

Now it has turned out that the chemical activity of the gases developed electrolytically runs parallel to these "overpressure" values. By choice of a suitable electrode (Zn, Hg, Pb) and application of high current densities the gas deposited behaves at the moment of origin in a chemical respect as though it existed under extremely high pressure, and there is the possibility of bringing about extraordinarily powerful effects by means of the electrolytically developed gas. This is of prime importance in electrochemical oxidation and reduction. Of the numerous examples pertaining here, mention will be made only of the reduction of carbonic acid to formic acid, which is practicable only on electrodes with high overpotential (lead and zinc), as well as the reduction of acetone to isopropyl alcohol, which requires the use of a mercury cathode.

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[1] G. Moller has offered some interesting experiments and calculations in support of the latter hypothesis (*Ann. Physik.*, **27**, 665 (1905)).

On the other hand, since the gas can be developed under an exceedingly small partial pressure by the use of potentials which lie below the decomposition potential, electrochemical oxidation and reduction permits one to bring every given effect within very wide limits by variation of the electrode material on the one hand and the potential on the other.

254. Electrochemical Passivity.—While obstructions appear in the electrochemical development of gases, which find their expression in overvoltage, some metals under certain conditions interpose a considerable resistance to their anodic conversion into ions, which is designated as passivity. Chromium passes over into the passive state especially easily, and iron, nickel, as well as the majority of noble metals, can also be made passive. A metal shows its passivity not alone in that it will not go into solution anodically on electrolysis, but it can be brought into acids of powerful oxidizing action, such as concentrated HNO_3, without dissolving in it. Many metals, such as chromium, even become passive even by lying in air, and must first be artificially activated by a powerful cathodic treatment, such as development of H_2 on the surface.[1]

Of the numerous possible explanations of passivity, the assumption of a surface layer which prevents the passage of the metal ions deserves most attention. The thickness of this intermediate layer is very minute, since the optical properties of most metals are not markedly changed by being made passive. No certain statement can be made regarding the constitution of the layer. There are various indications, however, that it consists of a very thin skin of condensed oxygen which is held either by purely physical absorption or in part also chemically by the formation of suboxides.

On the other hand, in many cases—for example, with aluminium and tantalum—the formation of a skin of oxide is clearly perceptible on the metal. These skins possess the peculiarity of presenting a very different resistance against the current in the two opposing directions. We can therefore use cells in which another electrode (carbon) is placed opposite an aluminium or tantalum electrode as a rectifier for alternate currents (the so-called Ventil cells). Günther-Schulze has instituted exhaustive theoretical and experimental investigations concerning the *Ventil action*.[1] According to him, it is probable that a very thin gas layer is formed between the metal and the precipitated skin. The passage of current through this possesses the character of that in a discharge tube which follows also from the appearance of numerous small sparks upon the electrode surface during the passage of current. Since the major portion of the conduction of electricity in gases devolves upon (see **286**) the mobile electrons and since further electrons can be more easily liberated from the metal (see **285**) than from the solution, the unipolar character of the conductivity of the electrode surface covered with a precipitated membrane cae be understood.

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[1] By alloying with chromium, the relatively weak passivity of iron is somewhat strengthened, so that the alloy withstands completely the oxidizing influence of O_2 and HNO_3. This phenomenon is the basis of the so-called stainless or non-rusting steels.

c. Thermodynamic and Kinetic Theories

255. Thermodynamic Theory of Reaction Velocity.—The attempt was made by Trautz to calculate the velocity coefficients k_1 and k_2 of a reaction from thermal data analogous to the equilibrium constant K. The division of Eq (234*d*) into two parts forms the starting point corresponding to the relation Eq. (245) $\log K = \log k_2 - \log k_1$.

$$\left.\begin{aligned} lnk_1 &= -\frac{H'_{01}}{RT} + \frac{1}{R}\sum C_{p01}\, lnT + \frac{1}{R}\Psi_1 + \sum i_1 + \kappa' \\ lnk_2 &= -\frac{H'_{02}}{RT} + \frac{1}{R}\sum C_{p02}\, lnT + \frac{1}{R}\Psi_2 + \sum i_2 + \kappa' \end{aligned}\right\} . \qquad (252)$$

If the difference $H'_{02} - H'_{01}$ is made equal to H_0', the heat content of reaction at absolute zero, and κ' represents a temperature function or constant which is the same in both equations, we return directly to Eq. (234*d*)

Doubtless a formal separation of Eq. (234*d*) into two terms is permissible However, the physical meaning of the values H'_{01} and H'_{02} involves a certain difficulty since in each of the two reactions $A + B \rightarrow A' + B'(k_2)$ and $A' + B' \rightarrow A + B(k_1)$, apart from universal constants, only terms which are independent of the other counter reaction should appear. Trautz claimed H'_{01} as the heat of formation of substances A and B, and H'_{02} as that of the substances A′ and B′ from some intermediate products whose appearance is to be assumed not only in the more complicated but even in the simplest reactions. For the quantity κ' Trautz assumed a universal constant value.

An experimental test of Eq. (252) meets with greater difficulties than the statistical Eq (234*d*), largely because there are so few serviceable measurements which apply to reaction velocity as compared to those for equilibrium. The nature of the intermediate products is often a matter of conjecture, but even if they were known it would not be possible to estimate the heats of reaction H_{01} and H_{02} by direct calorimetric measurement as with equilibria, they must be determined empirically, as a rule, from the temperature course of k_1 or k_2 according to Eq. (252).

Therefore, a final judgment concerning the validity of the theory is not possible at present. Empirical arguments may be considered which bear this out. If one assumes, for example, that the second member on the right side of Eq. (252) becomes of relatively little importance, then the formula of Arrhenius (Eq. (246)) is obtained which is well established empirically in many cases. But, on the other hand, the theory, apart from the theoretical considerations, does not always appear to be in accord with the facts For example, a higher value of H'_{01} corresponds according to Eq. (252) to a high value of the logarithmic temperature coefficient of k_1, since $\frac{d\ln k_1}{dT}$ is equal to $\frac{H'_{01}}{RT^2}$ by neglecting the second and third terms. Therefore, in biological reactions, which show abnormally high temperature coefficients for their velocity constants according to Table 60, H_0' must be especially large This scarcely appears probable, since in the majority of organic reactions the gross heat of reaction is relatively small, and one may assume that the heats of formation of the intermediate products which are identified by Trautz with H'_{01} and H'_{02} do not, at any rate, possess abnormally high values [1]

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[1] For details and earlier literature see *Z. Physik.*, **3**, 349 (1920).

256. Kinetic Theory.—The problem of calculating the absolute value of the reaction velocity of a gas reaction from molecular kinetic considerations has been attacked in various ways for a long time, particularly by Boltzmann [2] The complete calculation is usually not possible without special assumptions which rob the theory of its persuasive force; this is not astonishing in view of the differences and complicated nature of reaction-velocity phenomena (influences of catalysts).

On the other hand, if the consideration is confined to the kinetic explanation of the influence of individual factors on reaction velocity, a very satisfactory result is obtained. The first question involves an interpretation of the influence of concentration of the reacting substances upon the reaction velocity (Eq (241)).

That in a unimolecular reaction the velocity must be proportional to the number of molecules existing at any moment, and therefore to their concentration, has been discussed completely in **11.**

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[1] Complete literature and a short description of Trautz' theory, including criticisms, are to be found in K. F. HERZFELD'S paper, *Ann. Physik.*, **59**, 635 (1919).

[2] For literature up to 1913 see JELLINEK, "Physikalische Chemie der Gasreaktionen," p 722 *et seq*, Leipzig (1913). For later works reference may be made to STERN, O., *Ann Physik*, **44**, 497 (1912), HERZFELD, K. F., *Ann Physik*, **59**, 635 (1919); *Z Elektrochem*, **25**, 301 (1919); *Z. Physik*, **8**, 132 (1922), POLANYI, M., *Z. Elektrochem.*, **26**, 49, 228 (1920); *Z. Physik.*, **1**, 337 (1920).

In a bimolecular or higher-order reaction, the fundamental condition for a reaction is that the molecules of the reactants be brought into contact with one another or, expressed more generally, that they approach one another so closely that the chemical forces can manifest themselves. If it is assumed that the chemical forces can act only over a very short distance (in most cases this assumption proves to be correct), such a close approach of two molecules may correctly be designated as a collision. Therefore, at the most only as many reacting molecules can form end products as there are collisions. However, it is necessary to assume that a greater part of the collisions are often chemically ineffective and that only a fraction result in a chemical union. But this fraction must have a constant value for a definite temperature and the following equation is obtained:

$$\text{Reaction velocity} = \text{number of effective collisions} \sim \text{total number of collisions} \qquad (253)$$

Since, in general, the fraction $\dfrac{\text{number of effective collisions}}{\text{total number of collisions}}$ is not known, the knowledge of the absolute value of the total number of collisions for which a simple formula applies in the kinetic gas theory is of no value. Still the question of the dependence of the total number of collisions upon the concentration of the reacting substances can be answered without difficulty. In a bimolecular reaction two cases can be differentiated from one another:

1. The reacting molecules are alike (case of an association).
2. The reacting molecules are of different types.

In case 1 a single molecule will first be considered. The number of collisions[1] Z_1 which it suffers in unit time is, obviously, greater the greater the number of molecules present in the unit of volume. By doubling the number of molecules present or the mole number n, twice as many molecules encounter the molecule under consideration, *i.e.*, the number of collisions actually occurring is doubled; therefore, $Z_1 \sim n \sim c$ (since n is proportional to the concentration c).

This reaction which was first considered for a single molecule repeats itself for all of the above molecules. The total number of collisions Z_g amounts, therefore, to Z_{1n} and it follows that

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[1] The absolute value of this number amounts to $5 \cdot 10^9$ per second for air at 0° and atmospheric pressure.

$$Z_g = Z_{1n} \sim n^2 \sim c^2.$$

Therefore, by considering Eq. (253) the correct equation is obtained (see **232**):

$$\text{Reaction velocity} = kc^2.$$

2. In case the reacting molecules are of different natures and their number per unit of volume amounts to n_1 and n_2 and their concentrations, correspondingly, to c_1 and c_2, the following result is obtained: $n_1 + n_2$ molecules are present in the gas space, but for a reaction with a certain individual molecule it is not the collisions with the same type of molecules, but only with different types of molecules, which enter into consideration. Therefore, $Z_1 \sim n_2 \sim c_2$. Since the reaction repeats itself n times corresponding to the presence of n_1 molecules of the first type, it is found that $Z_g \sim n_1n_2$ and, therefore,

$$\text{Reaction velocity} = kc_1c_2.$$

In a trimolecular reaction the three molecules (A, B, C), which may also be of equal concentration, must come together simultaneously in order to effect a chemical combination. Since nothing can be said regarding absolute simultaneity, it is obvious that it is necessary first to define within what space of time a collision will be considered as simultaneous. The generalization of the cases 1 and 2 above offers no further difficulties. A definite number of molecules B and C will always be given which exist in the state of collision. Their number Z_{BC} is proportional to n_2 and n_3 and, indeed, this is greater the wider the interval of simultaneity chosen. The number Z_{BC} enters simply in place of the number Z_1 in case 1. If n_1 molecules of A are present, then the collisions of the molecule A are repeated n_1 times, *i.e.*, the total number of collisions Z_g is proportional to $n_1n_2n_3$. Since this depends upon the simultaneous encounters of three different molecules, the number of collisions, and therefore also the reaction velocity, is very much smaller than in cases 1 and 2. On account of their slowness, genuine trimolecular reactions are rare in nature.

The union of three molecules almost always occurs in several steps, which travel faster individually than the gross reaction. These are first the two steps A + B = AB; AB + C = ABC, though the reaction frequently also proceeds through other intermediate products. The frequency of the simultaneous encounter of four or still more molecules is so minute that hitherto a quadrimolecular course of reaction could not be observed, since reactions which should be quadrimolecular according to the gross equation always choose a course over some intermediate step.[1]

The very considerable influence of temperature upon the reaction velocity or the velocity constant k can, as a rule, be understood kinetically by means of a relatively simple assumption [2]

The molecules existing in a gas mixture possess different velocities and Maxwell's distribution law holds as well for the translatory motion as for the rotatory velocity, both of which are independent of one another. Now the fundamental assumption is that only those molecules react whose velocities lie above a certain limit. For example, then, two molecules will only overcome their zones of repulsion and unite chemically if their relative translatory velocities exceed a certain value V_0 [3]

The total number of molecules whose velocity lies above a critical value V_0 (*AB* in Fig. 13) is represented by the surface which is enclosed by the line *AB*, the abscissa axis, and the curve similar to that in **135.** Now it is recognized that this surface increases rapidly with increasing temperature and the more the limiting line *AB* is displaced toward lower velocity. Qualitatively, the rapid temperature increase of reaction velocity reverts to a characteristic of Maxwell's distribution law.

An exact quantitative calculation offers certain difficulties, for example, the equilibrium of the Maxwellian distribution is always disturbed by the reaction and therefore it is not strictly applicable in its classical form. If a relatively high value is attributed to the critical velocity V_0, then it can be shown that the factor $e^{-\frac{MV_0^2}{2RT}}$ relating to the temperature influence is decisive not only for the Maxwellian law but also for its integral between the limits V_0 and infinity. Therefore, one is entitled, at least approximately, to set the velocity constant k equal to

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[1] * **Luther** and **MacDougall** (*Z. physik Chem*, **62**, 199 (1908)) claim to have shown that the reaction $4H^+ + 2ClO_3^- + 2Cl^- \rightarrow 2ClO_2 + Cl_2 + 2H_2O$ is of the eighth order. **Judson** and **Walker** (*Trans Chem Soc*, **73**, 410 (1898)) concluded that the reaction $2H^+ + Br^- + BrO_3^- \rightarrow HBrO + HBrO_2$ is quadrimolecular, but becomes bimolecular with excess of H_2SO_4.

[2] See especially **Goldschmidt**, H., *Physik. Zeit.*, **10**, 207 (1909).

[3] That such zones of repulsion actually exist with monatomic molecules is doubtful, though not impossible. But for a reaction to occur in which polyatomic molecules participate the molecule must in every case be shattered, for which it requires a considerable quantity of energy, which can only be obtained by collisions with rapid molecules.

$$k = Const.\ e^{-\frac{MV_0^2}{2RT}} \tag{246a}$$

or

$$lnk = -\frac{MV_0^2}{2RT} + ln\ Const = -\frac{A}{T} + B,$$

that is, we return again to the formula of Arrhenius, which is well verified empirically and whose constant A now obtains a physical meaning, namely, the quotient of the effective energy of one mole divided by the limiting velocity V_0 and the gas constant.

While in the union of two molecules their relative translatory velocity approaches a critical limiting velocity, the dissociation of a molecule into two or more atoms is probably dependent upon a limiting value of the rotational velocity (see KRUGER, F., *Gott. Nachr* 1, (1908), given in detail in JELLINEK, "Gasreaktion," page 723 *et seq*), then the greater the rotational velocity the greater the centrifugal force becomes. As soon as the rotational velocity exceeds a certain limit ω, the chemical forces of valence are overbalanced by the centrifugal force and the molecule dissociates. Now Maxwell's distribution law retains the same general form for the rotational velocity as for the translational velocity, only $\frac{J}{2}\omega_0^2$ enters for the rotational velocity in place of $\frac{1}{2}MV_0^2$ J is the moment of inertia per mole and both expressions represent the kinetic energy. On the separation of the atom the rotational velocity is partly converted into translational velocity and partly into potential energy. During the separation of the atoms one from another a certain amount of work is done against the chemical forces of attraction.

In case it is assumed that the molecules after a complete separation possess no further velocity relative toward one another, then the kinetic energy $\frac{J}{2}\omega_0^2$ is completely transformed into potential energy. This, therefore, represents the total energy to be applied to the separation of the atoms and is, in general, to be identified with a negative heat of dissociation, or, if the reaction is viewed in the reverse way, as the heat of union of the atoms H'_{01}. For the reaction velocity we now obtain in complete analogy to Eq. (246a)

$$lnk = -\frac{J\omega_0^2}{2RT} + B = \frac{H'_{01}}{RT} + B.$$

With this the connection is made, at least for the simple case of a monomolecular reaction, with the result of **255**, and, therefore, with the fundamental thermodynamic Eq. (234) or its integral Eq. (234d).

The preceding consideration is most probably to be generalized in so far as the dissociation energy of the decomposition can be stored up not only as rotational energy, but also as some other form within the molecule.[1] Now the origin of this energy can only be due to a foreign molecule, provided the absorption of radiant energy is excluded, *i.e.*, before a molecule dissociates a collision must have occurred with another molecule especially rich in energy. Conversely, if two atoms unite to form a molecule, their mutual potential energy is obviously converted into other forms of energy which at first remains within the newly formed molecule. Now, since at any time a reverse change in potential energy can occur (by separation into atoms), the molecule existed in a very labile stage in the beginning. Only when the decomposition energy is transmitted by collision with a foreign molecule can the final formation of the molecule be considered complete. Now if the molecule always retains its labile state of high energy content for only a very short time, then its dissociation as well as its formation must occur practically simultaneous with the collision of an energy-transmitting molecule if a reaction is to occur at all. According to this, every decomposition of a molecule would be represented theoretically as a bimolecular reaction instead of a unimolecular one and every formation from two atoms as a trimolecular reaction instead of a bimolecular one. (See HERZFELD, C. F., *Z Physik*, **8**, 132 (1922).) However, many phenomena indicate that a molecule may even retain a greater energy than its heat of decomposition without a dissociation appearing for a period of time of about 10^{-8} *sec.* (see page 543, footnote).

* An excellent discussion of the status of the radiation theory is given in *Trans. Faraday Soc*, **17** (1922). See also TOLMAN, *J. Am. Chem. Soc*, **42**, 2506 (1921), **43**, 269 (1922), **45**, 2285 (1923); DUSHMAN, *ibid*, **43**, 397 (1921), LANGMUIR, *ibid*, **42**, 2190 (1920); LEWIS, W. C, and McKEOWN, *ibid*, **43**, 1288 (1921); CHRISTIANSEN, J. A., and KRAMERS, H. A., *Z. physik Chem*, **104**, 451 (1923). LEWIS. G. N., and SMITH, D F, *J. Am. Chem Soc*, **47**, 1508 (1925) and TOLMAN, *ibid*, **47**, 1524 (1925).

[1] As shown by numerous phenomena mentioned in Sec D, the molecules as well as the atoms exist not only in a stable normal state but also in a series of labile excited states of different energy levels.

SECTION D

THE STRUCTURE OF MATTER

257. Synopsis.—A large part of the two preceding sections has already been devoted to the question of the structure of matter The fundamental laws indicate that matter is composed of small individual units, or "building blocks," which are called atoms. To a large extent, the experimentally observed phenomena of both physics and chemistry may be explained by means of two assumptions: (1) when atoms are very close together they repel each other, but at somewhat greater distances they attract; (2) atoms are in a state of rapid (vibratory or translatory) motion, at least at higher temperatures.

In the following the atom itself will be considered as a unit. The nature of its attractive and repulsive forces will be studied particularly, including the chemical forces, but, in general, all effects due to the heat motion of atoms will be neglected. In other words, it will be assumed that the substance under investigation is at a relatively low temperature. In many cases this will simplify problems very much; for example, if the heat content of reaction and the maximum work can be considered equal to each other, the term $T\left(\frac{\partial A_{T\,v}}{\partial T}\right)_v$ in Eq. (52) may be neglected

Experience forms the basis for determining the properties of atoms. Therefore, there will first be an attempt to draw some conclusions as to the behavior of single atoms from experimental results, even though the experiments have involved very large numbers of atoms (Part 1). For a deeper knowledge of the structure of the atom, these empirically discovered properties are not sufficient. We shall try to decompose the atoms into simpler constituents (Part 2) and to learn the laws governing the products of decomposition and their formation (Part 3). From a use of the knowledge thus obtained, it should be possible to construct models of the atoms. If the model obtained for an atom is a correct representation of the actual structure, it should be possible to calculate from it (even though indirectly) the same properties which were experimentally observed on the atom itself. In particular, it should be possible to understand and to calculate from the model those physical and chemical forces by which atoms link together to form crystals and molecules. The extent to which our present knowledge enables us to do this is indicated in Part 4

It may be noted that, even at the present time, the investigations of the constitution of atoms allow us to look back upon some very remarkable successes. There already exists extensive and convincing material concerning the nature and the number of the decomposition products of single atoms. The fundamental laws of the effect of atomic decomposition products upon each other and upon the surroundings ("the luminiferous ether") also appear, on the whole, to be correctly grasped, even though the conceptions are lacking in details. Some simple atomic models have been constructed which, in a number of respects, especially the optical properties, agree excellently with the experimental facts. On the other hand, the problem of calculating, from the atomic model, the mutual force effects of atoms during the formation of molecules involves great difficulties which as yet have not been completely overcome.

Since modern atomic investigation has assumed, in part, a purely physical and even mathematical-physical character, in the following some of the special fields can be only briefly discussed in reference to their most important results [1]

1. EMPIRICAL (DIRECT) PROPERTIES OF THE ATOM

258. Direct Atomic Properties.—The observed physical or chemical properties of a substance may all be strictly referred back to its atomic constituents; *i.e.*, as a matter of principle, even a macroscopically observable property is determined by the properties of the atoms contained in the substance. In order to obtain most directly a knowledge of the actual properties of the atoms, it is convenient to consider first those properties which are not at all, or at most very slightly, influenced by mutual linkage or other reciprocal actions (*e.g.*, collision) between atoms, and which therefore directly reflect the properties of the individual atoms. Such properties will in the following be called **direct atomic properties.**

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[1] The most exhaustive work on the subject of atomic structure is given by SOMMERFELD, A., "Atomic Structure and Spectral Lines," translated by H. BROSE, E. P. Dutton & Company, New York (1923). More limited presentations, each of which has certain distinguishing characteristics in treatment, viewpoint, and emphasis, are given by FOOTE and MOHLER, "The Origin of Spectra," Chemical Catalogue Co., (1922), ANDRADE, "The Structure of the Atom," Bell, London (1923); LORING, "Atomic Theories," Methuen, London (1921); KRAMERS and HOLST, "The Bohr Theory of the Atom," translated by R. B. and R. T. LINDSAY, Alfred A. Knopf, New York (1923).

259. Law of the Constancy of Mass.—One of the best examples of a direct atomic property is mass. That the masses of the atoms are independent of the manner in which they are linked together—therefore, that the mass of a chemical compound is equal to the sum of the masses of its atoms—is the essence of one of the fundamental laws of chemistry, *the law of constancy of mass.* This was first expressed by Lavoisier (1785). Landolt[1] on the basis of very exact experimental investigations, applying all the modern methods available at the time, established this law with sufficient accuracy to warrant the statement that in a chemical reaction with a molecular heat of reaction of several thousand calories (maximum 20,000 *cal.*) the possible change of weight corresponding to this change of energy is certainly smaller than the limits of error in his measurements (approximately 0.003 *mg.*). Nevertheless, from the results of the Einstein relativity theory it can scarcely be doubted that the *law of the constancy of mass is anything other than a limiting law for small energy changes.* As Einstein has shown, it must be assumed that energy in any form possesses a certain inertia, and therefore the expression

$$U = mV_l^2 \qquad (254)$$

must hold.[2]

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[1] Abhandl. Deut. Bunsengesell., Nr. 1, Halle (1908), *Z. physik. Chem.*, **55**, 589 (1906).

[2] * Of the numerous books on relativity, the following may be mentioned:

EINSTEIN, A., "Theory of Relativity," Methuen (1924), translated by LAWSON. A popular exposition with a short list of reference books.

EINSTEIN, A., "Meaning of Relativity," Methuen (1922), translated by ADAMS. Lectures given at Princeton, 1921.

FREUNDLICH, E., "Theory of Relativity," Methuen (1924), translated by BROSE. Three lectures for chemists.

If during a reaction a chemical system loses an amount of heat energy U, then the total mass must have decreased according to $\frac{U}{V_l^2}$. If we calculate the change of mass corresponding to a molecular heat of reaction such as was found in the reactions observed by Landolt (20,000 *cal.* = $8 \cdot 10^{11}$ *erg*), a decrease in mass of only

$$\frac{8 \cdot 10^{11}}{9 \cdot 10^{20}} \simeq 0.9 \cdot 10^{-9}\ g. = 0.9 \cdot 10^{-6}\ mg.$$

is to be expected, which is far below the limit of error given by Landolt.

Although Einstein's conclusions, according to which the inert mass of the body is possibly limited by its energy content alone, are valid, it is of greater significance, theoretically, that the actually observable effects are so slight that it seems justifiable to use the concepts of inert mass and energy separately for energy changes of the order of magnitude of those observed in chemical reactions. and to retain the law of constancy of mass in its earlier form.

260. Periodicity of Chemical Properties.—Since it is obvious that the mass or weight is a fundamental property of the atom, attempts have been made to compare various atomic properties with the atomic weight in order to discover whether any empirical regularity existed.

Among the various typical properties of the atoms, we are first interested in the chemical properties, since these show clearly observable differences between the various individual atoms. It is not even necessary to represent the chemical properties by numerical magnitudes; it is sufficient to arrange the elements in the order of their atomic weights (later on certain minor inversions will be considered). This shows that elements with analogous chemical properties appear at apparently regular intervals. For example, the elements 2, 10 (8 + 2), 18(10 + 8), 36(18 + 18), 54(36 + 18), and 86(54 + 32) are all chemically inert (the noble gases). Elements 3, 11, 19, 37, and 55 are strongly electropositive (the alkali metals), while 9, 17, 35, and 53 represent strongly electronegative elements (the halogens). The chemical properties of the elements arranged in a series according to their atomic weights thus show a decided periodicity. A table may therefore be made in which the elements with similar chemical properties, and particularly those with equal valences (positive or negative),[1] fall under each other (Table 65), so that the periodic recurrence of a definite chemical property is plainly shown. (**The periodic table of the elements.** Lothar Meyer, 1864; Mendelejeff, 1869.) If an element appears in various stages of valence, the valence value indicated in the table represents, in general, either an upper or a lower limit which is sometimes attained with great difficulty. The periodic table contains several gaps; these are obviously due to elements which have not yet been discovered.[2]

In Table 65 a number of elements which can be claimed to be chemically different are found in the same column (*e.g.*, the metals Cu, Ag, and Au in the column of the alkali metals). To indicate that this difference exists, such elements are not written exactly under each other. In order that the differences might be more clearly expressed, numerous other arrangements have been proposed, some of them involving three dimensions, and only those elements which really can claim chemical relationship appear under each other. These methods, in spite of their advantages, have not as yet been generally adopted.[3]

Although strict regularites are to be perceived in the periodic system, there are also, as previously mentioned, certain inversions in the series when the elements are arranged according to atomic weight (Ar-K; Co-Ni; Te-I). Therefore, it is obviously necessary to regard the system thus obtained as the natural one, and to ascribe the proper theoretical significance to these inversions. If each place in the table is indicated by a number, and the elements are placed in their proper places in a new series with regard to their chemical characteristics, a series is obtained which at least gives a preliminary indication of a fundamental atomic constant to which the above properties may be referred. Thus for

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[1] A single positive valence means the ability to form a positive ion (cation) with one positive charge, etc.

[2] When the periodic system was first developed the number of these gaps was considerably greater than at present The properties of several of the missing elements could be (and were) correctly predicted from the periodic table.

[3] A discussion of various systems will be found in the monograph by C. SCHMIDT, "Das periodische System der chemischen Elemente," Leipzig (1917). * See also HARKINS and HALL, *J. Am. Chem. Soc*, **38**, 169 (1916).

TABLE 65.—THE PERIODIC SYSTEM OF ELEMENTS

Period	Group 0 (VIII)	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII			
0		**1** H 1 008									
I	**2** He 4 00	**3** Li 6 94	**4** Be 9 02	**5** B 10 82	**6** C 12 00	**7** N 14 01	**8** O 16 00	**9** F 19 0			
II	**10** Ne 20 2	**11** Na 23 00	**12** Mg 24 32	**13** Al 27 0	**14** Si 28 3	**15** P 31 04	**16** S 32 07	**17** Cl 35 46			
III	**18** Ar 39 88	**19** K 39 10	**20** Ca 40 07	**21** Sc 45 1	**22** Ti 48 1	**23** V 51 0	**24** Cr 52 0	**25** Mn 54 93	**26** Fe 55 85	**27** Co 58 97	**28** Ni 58 68
		29 Cu 63 57	**30** Zn 65 37	**31** Ga 69 9	**32** Ge 72 5	**33** As 74 96	**34** Se 79 2	**35** Br 79 92			
IV	**36** Kr 82 92	**37** Rb 85 45	**38** Sr 87 63	**39** Y 88 7	**40** Zr 90 6	**41** Nb 93 5	**42** Mo 96 0	**43**—	**44** Ru 101 7	**45** Rh 102 9	**46** Pd 106 7
		47 Ag 107 88	**48** Cd 112 42	**49** In 114 8	**50** Sn 118 7	**51** Sb 121 8	**52** Te 127 5	**53** I 126 92			
V	**54** X 130 2	**55** Cs 132 81	**56** Ba 137 37	**57-71**** 139–175 0	**72** Hf 178 6	**73** Ta 181 5	**74** W 184 0	**75**—	**76** Os 190 9	**77** Ir 193 1	**78** Pt 195 2
		79 Au 197 2	**80** Hg 200 6	**81** Tl* 204 4	**82** Pb* 207 20	**83** Bi* 208 0	**84** Po* (210 0)	**85**—			
VI	**86** Rn* (222 0)	**87**—	**88** Ra* 226 0	**89** Ac* (227)	**90** Th* 232 12	**91** Pa* (230)	**92** U * 238 2				

The atomic number appears beside the symbol for each element, the atomic weight below The atomic weights of Po, Rn, Ac, and Pa are calculated values At the places marked * are to be assigned a number of other elements, for the most part radioactive, which have the same chemical properties as the element in the table but somewhat different atomic weights (see **275**).

** The rare-earth group

this purpose the atomic weight becomes of minor importance and there is substituted for it the **atomic number,** *the number of the position of the element in the table.* The physical significance of the atomic number in its relation to several properties will be discussed in the following.

261. Volume and Diameter of Atoms.—The relation between the volumes of atoms and their atomic numbers is worthy of special note.

Strictly speaking, the volume of an atom is not a direct atomic property, since the volume actually measured depends not only upon the volume of the atoms themselves, but also upon the space between them. As will be shown in the following, in the solid state of aggregation the distance between the "outer surfaces" of the atoms is relatively small compared with the accepted atomic diameters, so that *the volume of a solid body must at least approximately correspond to the combined volumes of its constituent atoms alone.*

If for the present we retain the assumption that, as a first approximation, atoms can be considered as rigid elastic spheres, then the true diameters of the spheres can be calculated by various methods. A particularly simple method is derived from the considerations in **136.** We must try to find.

1. The absolute magnitude of distance Δ between the centers of neighboring atoms in the position of rest or, more accurately expressed, the distance between the centers of vibration.

2. The distance $\rho\Delta$ between the surfaces of the atoms in the crystallized element. Then the atomic diameter 2σ is given simply by

$$2\sigma = \Delta(1 - \rho) \text{ (compare Fig. 33, page 196).}$$

In order to determine the distance between the centers of vibration of adjacent atoms, the positions of the atoms in the crystal must be known. It may be assumed, at least in certain cases, that an atom is bound equally to all the atoms adjacent to it and that, in agreement with **76,** we are considering a "simple solid body." These relations are most clearly seen when all the atoms are situated at the corners of a cube (cubic lattice, Fig. 90). In this case the length of the cube edge is simply equal to the mean distance Δ between the atoms. We can thus think of a cube of an edge Δ in length being constructed about each atom.

A gram atomic weight consists of **N** such cubes, and for those atomic volumes v_A, which are open to direct determination, we get

$$\mathbf{N}\Delta^3 = v_A \quad \text{or} \quad \Delta = \sqrt[3]{\frac{v_A}{\mathbf{N}}}. \tag{255}$$

For a face-centered cubic arrangement (Fig. 91), we find

$$\Delta = \sqrt{2}\sqrt[3]{\frac{v_A}{2\mathbf{N}}}, \tag{255a}$$

for a cube-centered (or body-centered) arrangement (Fig 92),

$$\Delta = \sqrt{\frac{3}{4}}\sqrt[3]{\frac{2v_A}{\mathbf{N}}}, \tag{255b}$$

finally, for a tetrahedral arrangement (Fig. 93),

$$\Delta = \sqrt{\frac{3}{4}}\sqrt[3]{\frac{v_A}{\mathbf{N}}}. \tag{255c}$$

The assumption that the atoms are bound equally in all directions holds for a number of elements and the values of Δ as determined from Eqs. (255) are summarized in Table 66, column 6. These values were obtained from the X-ray analysis of the crystal structures (see **384**). The value of Δ for diamond and for silicon was calculated according to Eq. (255*c*), for most of the metals by Eq. (255*a*), and the remaining ones (Na, K, Fe) by Eq. (255*b*). For argon, the atomic arrangement of which has not yet been investigated, Eq. (255) was used.

According to Lindemann's conception of the process involved in the melting of solids (see **136**), the distance between the atomic surfaces is simply equal to twice the amplitude of vibration of the atom at the melting point (Fig. 33). The absolute magnitude of the mean vibration amplitude x of an atom may be calculated, provided the frequency ν_0 and the total vibrational energy U_{mp} are known. The law of energy partition, which may be assumed to hold approximately for the higher temperatures, states that the energy kT is inherent in each vibration (per degree of freedom) at the temperature T; on the other hand, the vibrational energy U_{mp} is equal to the potential energy at the turning point[1] (compare Eq. (92), page 107). We have, therefore,

$$kT = U_{mp} = \frac{bx^2}{2}.$$

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[1] * *I.e.*, where the atom has traveled its maximum distance from its equilibrium point.

The quantity b may be found from ν_∞ according to Eq. (31), page 28, thus:

$$b = m4\pi^2\nu_0^2.$$

We obtain, therefore, for the amplitude of vibration at any temperature:

$$x = \sqrt{\frac{kT}{2\pi^2 m\nu_0^2}} = \sqrt{\frac{8.31 \cdot 10^7 T}{2\pi^2 A\nu_0^2}} = 0.205 \cdot 10^{-8}\sqrt{\frac{T}{A(\nu_0 10^{-12})^2}},$$

in which $k\mathbf{N} = R = 8.31 \cdot 10^7$ and $m\mathbf{N} = A$(atomic weight).

The distance $\rho\Delta$ is found by doubling the value of x when T is the temperature of melting. In this way the values of $\rho\Delta$ given in Table 66, column 7, were found; $\nu_0(\simeq\nu_l)$was calculated from the change of specific heat with temperature, or the **characteristic temperature** Θ according to **61, 79,** and **134.** The table shows that the mean distance between the "surfaces" of two adjacent atoms is about 10 per cent of the total distance between the atomic centers, while the atomic diameter 2σ is about 90 per cent of this distance.

All the other possible methods, which lead to absolute values of the atomic diameters, belong exclusively in the realm of kinetic gas theory For example, if the van der Waals' constant b should be equal to four times the true volume of the atoms or molecules, then the atomic or molecular diameters can also be obtained from the mean free path (see **53**).[1]

Since the use of these methods assumes a knowledge of several physical constants which refer to the gaseous state, the methods have not been applied to the majority of elements given in the table. From the mean free path of argon we obtain $2\sigma = 2.9 \cdot 10^{-8}$, which is in satisfactory agreement with the value in Table 66. (*Cf.* EUCKEN, A., *Physik. Zeit.*, **14,** 324 (1923).)

The considerations indicated above may be objected to on the ground that the fundamental assumption that the atoms behave as rigid elastic spheres is certainly not wholly correct. This is emphasized not only in the earlier considerations of the subject, but also in what is to follow. The atomic structures, as

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[1] * Further information concerning this may be found in textbooks on the kinetic theory of gases: JEANS, "The Dynamical Theory of Gases," chap. XIV, Cambridge University Press (1916); KLEEMAN, R. D., "A Kinetic Theory of Gases and Liquids," John Wiley & Sons, Inc. (1920); BOYNTON, W. P., "Kinetic Theory," The Macmillan Company (1904).

TABLE 66.—ABSOLUTE VALUES FOR THE ATOMIC DIAMETERS 2σ

Element	Θ	$\nu \cdot 10^{-12}$	$T_{m.p.}$	v_l	$\Delta \cdot 10^8$	$\rho\Delta \cdot 10^8$	$2\sigma \cdot 10^8$
C	1860	39	abt 4500	3.4	1.53	0.13	1.10
Na	162	3.4	371	23.7	3.71	0.48	3.23
Al	398	8.30	930	10.2	2.87	0.28	2.59
Si	abt 500	10.5	700	12.3	2.25	0.30	1.95
Ar	85	1.78	85	abt 26	(3.50)	0.33	3.17
K	70	1.46	336	45.3	4.62	0.80	3.82
Ca	210	4.40	1043	25.9	3.91	0.47	3.47
Fe	453	9.50	1818	7.11	2.50	0.24	2.31
Cu	315	6.60	1357	7.11	2.55	0.28	2.27
Ag	215	4.50	1234	10.25	2.88	0.31	2.57
Cd	172	3.60	595	13.00	3.12	0.26	2.86
Hg	97	2.03	234	14.7	3.24	0.22	3.02
Tl	96	2.01	575	17.1	3.40	0.33	3.07
Pb	88	1.84	600	18.2	3.49	0.38	3.11

they are at the present time assumed to appear (see **295**), scarcely allow the "size" of individual atoms to be exactly defined. At the most, they give only the mean radii of the outer electronic orbits which, in general, are considerably smaller than the values of σ from the tables (approximately one-half). In many observations which are concerned with the "size" of the atoms, it is really not the size of the material structure which is involved, but *only the range of the atomic forces.* It is, therefore, appropriate to introduce the idea of the **sphere of influence** of atomic forces, and to substitute the diameter of this sphere for the atomic diameter. To begin with, it may be easily understood that the diameter of the atomic sphere of influence may be defined in various ways. *In the present case it will designate the minimum distance which can exist between two atoms approaching each other at normal molecular velocities.* The above considerations and calculations can then remain unchanged, but σ means the radius of the sphere of influence. It is to be observed that, strictly speaking, the values of σ must now be assumed to be a function of the temperature, since the atoms in their collisions at higher temperatures must strike each other more forcibly than at lower temperatures, due to their greater molecular velocities. The temperature coefficient of σ is relatively small, however, so that it was not of sufficient importance to make the correction for it in the values given in Table 66.

Since in Table 66 the ratio of the distance between the atomic surfaces to the atomic diameter is, indeed, small and, besides, is approximately constant, *we can view the directly measurable atomic volume of chemical elements in the solid state* (*i.e., the the volume of a gram-atom*) *as at least an approximate measure of true volume of the atom*, and in this manner compare, with respect to the sizes of their atoms, such elements as do not permit a more accurate calculation of their atomic diameters.

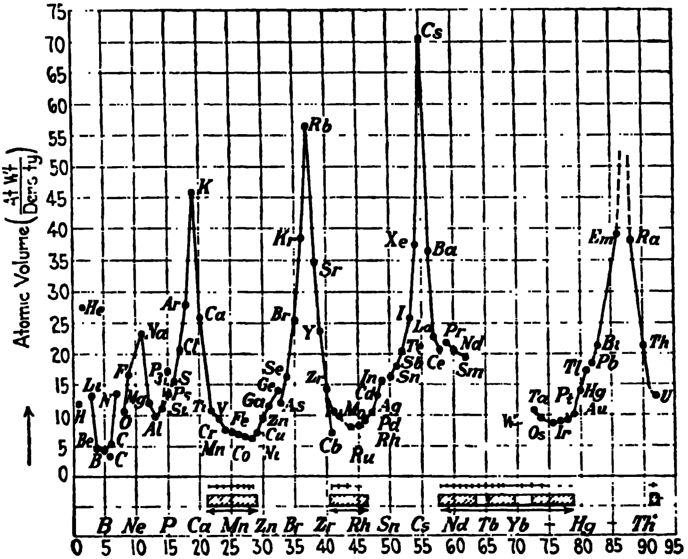

Fig 57

+++++ paramagnetic, ▨ colored ions,

⟷ incomplete inner shells with loosely bound electrons

If the atomic volumes of the elements in the solid state are plotted as a function of the atomic number, the curve given in Fig. 57 is obtained, which shows a decided periodic or wave-like form. Further, *it indicates that chemically related elements occur in analogous positions on the curve.* This fact is particularly evident in the alkali metals, whose atoms are distinguished by their unusually large size.

262. Further Periodic Properties.—Similar to the chemica properties, a number of physical properties besides the volum show a certain periodicity when the elements are arranged in series according to atomic weights. This fact indicates that the chemically related elements are also physically analogous.

One of the most important of these physical properties is the line spectrum, which was recognized at the time of its discovery (Bunsen, Kirchhoff, 1860) as a typical atomic property. Later (see **304** *et seq.*) the related properties and the significance of the line spectrum in the knowledge of atomic structure will be more fully discussed. At this time it may only be pointed out that between the structures of the line spectra of the chemically similar elements there exists a definite relationship. For instance, even though the line spectra of the alkali metals are characterized by the simplicity of their structures, double lines (doublets) regularly appear in them together with the single lines. In the spectra of the alkaline earth metals, which are already more complicated, triple lines (triplets) can be observed, etc. As one proceeds from left to right in the periodic system of elements, the number of spectral lines increases and the spectra become more complicated. The spectra of all the noble gases, except He, also have many lines and are difficult to comprehend clearly.

Among other physical magnitudes which show a certain periodicity may be mentioned: the melting point, the volatility, the atomic frequency, the electrical conductivity, compressibility, etc.[1]

263. Non-periodic Properties.—In striking contrast to the periodic properties of the elements, the X-ray spectrum, which is characteristic for each individual element (see **322** to **326**), is qualitatively of absolutely the same type for all the elements. The differences in the X-ray spectra of the various elements are primarily quantitative in nature; the structure of the spectrum is nearly the same for all the elements, only the wave lengths of the individual lines being different. The X-ray spectra of the elements, arranged in a series according to their atomic numbers, change step by step, from element to element, only in one direction (therefore not periodically) in a simple, regular manner. (The frequency of a particular line is very nearly proportional to the square of its atomic number.)

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[1] See BILTZ, W., *Z. Elektrochem.*, **17**, 670 (1911); *and especially RICHARDS, T. W., *J. Am. Chem. Soc.*, **37**, 1643 (1915).

264. Properties Due to the Periphery and to the Center.—The difference between the periodic and the non-periodic atomic properties suggests that the origin of these properties is to be sought for in different parts of the atom. The fact that the volume or the diameter of the atom, or, in other words, its outer limits, represents a periodic function indicates that *the periodic properties are localized in the periphery of the atom. The properties which are not periodic must, therefore, be ascribed to the central portion.*

The distinction between peripheral (periodic) and the central (non-periodic) atomic properties will be shown in the following to be a valuable one.

2. THE DISINTEGRATION OF ATOMS

a. The Decomposition Products of Atoms on the Basis of the Older, Indirect Knowledge

265. Prout's Hypothesis.—Although the idea that the atoms were built up of smaller units, and therefore were at least theoretically decomposable, contradicted the original conception of the nature of atoms (indivisibility), the theory received support, apart from purely speculative hopes, from the simple fact that *the atomic weights of a large number of elements were very nearly whole numbers.* Now, since the hydrogen atom represents the unit of atomic weights, although only an approximately accurate unit according to the present manner of calculation, it was easy to consider that all elements were built up of hydrogen atoms (Prout, 1815). The whole numbers found for the atomic weights of the lighter elements (*e g* , up to sulfur) were especially striking.

Taking the difference between the atomic weights of consecutive elements (excepting the very first elements and the abnormal nitrogen), differences of about one unit, alternating with larger differences of about three units, are found so that the sum of the two differences totals about four units. It is worth noting that these total differences of four units, in general, are more nearly four than either of the individual differences are one or three. Since the number four represents the atomic weight of helium, it seems justifiable, even at this point, to make the supposition that the difference between each second element corresponds to

TABLE 67.—DIFFERENCES BETWEEN THE ATOMIC WEIGHTS OF THE FIRST SIXTEEN ELEMENTS

Element	Atomic weight A	$A_{n+1} - A_n$	$A_{n+2} - A_n$
H	1 008	2 992	
He	4 00	2 94	5 93
Li	6 94	2 08	5 02
Be	9 02	1 80	3 88
B	10 82	1 18	2 98
C	12 0	2 01	3 19
N	14 01	2 00	4 01
O	16 00	3 00	5 00
F	19 00	1 2	4 20
Ne	20 2	2 8	4 0
Na	23 00	1 32	4 12
Mg	24 32	2 78	4 10
Al	27 1	1 2	3 98
Si	28 3	2 74	3 94
P.	31 04	1 03	3 77
S.	32 07		

a helium atom, and therefore that the helium atom plays the rôle of a building block in other atoms, although helium could quite evidently be considered as being built up of four hydrogen atoms This supposition is amply substantiated by the radioactive phenomena.

b. THE ATOMISTIC STRUCTURE OF ELECTRICITY

266. General Considerations.—Before proceeding to the consideration of the newer experimental results upon the decomposition of atoms, the general fact must be emphasized that the decomposition of an atom involves the appearance of a free electrical charge.

For what is to follow, it is important to bring up the question of the magnitude of this charge and to establish the fact that in atomic or similar processes no optionally small amounts of electricity can be involved, but that electricity, similar to matter, possesses a certain limit of divisibility or, in other words, it has an atom-like structure. The smallest free existing particle or atom of electricity is designated as the *elementary charge of electricity;* it is a universal constant of nature and, as will be seen, is of fundamental importance.

267. Atomistic Structure on the Basis of Faraday's Law.—As has already been emphasized in **182,** Faraday's law forms one of the most important foundations for assuming that electricity has an atomistic structure. Helmholtz, who first clearly expressed this view in his Faraday Lecture in 1881, used the following words: "If we make the assumption that simple substances are composed of atoms, we cannot avoid the conclusion that electricity, positive as well as negative, decomposes into definite elementary particles which behave as electrical atoms." If Avogadro's number **N** is known, the size of the elementary charge of electricity can be found directly from Faraday's law.

Since in electrolysis every gram-equivalent weight involves an amount of electricity equal to 96500 *coulombs* (1$\mathfrak{F}$), the amount of electricity bound up with each single monovalent atom (ion), *i.e.*, the elementary charge of electricity, amounts to

$$e_0 = \frac{96500}{\mathbf{N}}\ \textit{coulombs} = \frac{9650}{\mathbf{N}} \cdot \text{absolute electromagnetic units} \quad (e\,m.u\,)$$

$$= \frac{28.95 \cdot 10^{13}}{\mathbf{N}}\ \text{absolute electrostatic units } (e\,s\,u\,).^{1} \qquad (256)$$

In case it is possible to measure e_0 directly, the magnitude of Avogadro's number **N** can be estimated.

However, the argument that Faraday's law (in connection with an atomistic structure of matter) demands the existence of a definite elementary charge of electricity is not yet quite convincing. Since electrolysis is always concerned with the deposition of a large number of atoms or ions, there exists the possibility that not every individual atom possesses the same amount of electricity, so that the value e_0 obtained by Eq. (256) represents only a mean value, while the single atoms carry variable charges.

Such a case, for example, exists in the distribution of the velocities of molecules. It is known that the individual molecules possess different velocities, whereas in almost all observable

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[1] The electromagnetic unit in the absolute system is 10 *coulombs*, the electrostatic unit is smaller by the factor V_l, the velocity of light; $V_l = 3 \cdot 10^{10}$ *cm./sec.*

phenomena it is only the average molecular velocity which effects the actual results.

On the basis of a series of investigations to be presented a little later, the conception of e_0 as a mean value may be refuted; however, even from purely electrolytic investigations, it at least appears improbable that similar individual ions should carry different charges. For example, in the investigation described in **183** concerning the velocity of migration of MnO_4 ions in an electric field, the boundary between the colored and uncolored solutions must rapidly fade if certain of the ions, due to greater charges, could travel faster than others. Nevertheless, if it is desired to retain the view that the elementary charge is nothing but an average value, the only remaining escape is the assumption, which appears improbable from the very first, that the individual ions do, indeed, possess different charges, but that these charges are being continually transferred back and forth among the various atoms, so that e_0 represents a temporary mean value for single molecules also.

268. The Direct Measurement of the Elementary Charge of Electricity.—One of the best evidences for the atomistic structure of electricity, which at the same time involves very little in the way of hypothesis, depends upon the following investigation by Millikan. It is also the most accurate, direct method of determining the value of e_0, and therefore the Avogadro number **N** can be obtained according to Eq. (256).[1]

A fog of very small oil drops is produced between two horizontal metal plates which can be electrically charged. These are brightly illuminated and observed through a microscope whose magnifying power is great enough to permit a single droplet to be observed readily. Under the action of gravity these particles gradually settle down; the limiting velocity which a droplet of mass m attains, when the frictional resistance is f, follows from Eq. (28*a*)

$$v_0 = \frac{\mathfrak{K}}{f} = \frac{gm}{f}. \tag{257}$$

If the fog is now illuminated for a short time by X-rays, the air is ionized and some of the cloud particles acquire electrical charges. An electrical charge is now given to the two metal plates, so that a potential difference X exists between them. Those droplets which have acquired electrical charges are now influenced by both gravity and an electrical field (of the strength X), and, therefore, assume other velocities ($v_1, v_1' \ldots$). If the electrical force is opposed to and greater than the gravitational force, a droplet will ascend, and for its velocity we get

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[1] See MILLIKAN "The Electron," University of Chicago Press (1917); *Phys. Rev.*, **32**, 349 (1911), **2**, 109 (1913).

$$v_1 = \frac{Xe_x - gm}{f}, \tag{257a}$$

where e_x is the charge on the particle By combining Eqs. (257) and (257a) the frictional force f is eliminated and the result is

$$\frac{v_1}{v_0} = \frac{Xe_x - gm}{gm}. \tag{257b}$$

If a single particle is observed for a long time, it may be seen occasionally to change its charge suddenly from e_x to e'_x. Its velocity changes from v_1 to v_1', but Eq. (257a) still holds, since the mass m is unchanged. The relation between the two charges, therefore, is given by

$$\frac{e_x}{e_x'} = \frac{v_1 + v_0}{v_1' + v_0}. \tag{257c}$$

Thus the various charges on the particles are related to each other in proportion to their velocities in an electric field, each of these velocities being increased by the simple gravitational velocity v_0.

The investigation was so performed that the particle fell a number of times between two definite marks, and was made to ascend again by applying the electrical field. A typical series of results from Millikan's work[1] is given in Table 68.

These results show very clearly that the velocities do not change continuously, but in abrupt steps. From this it must be concluded that the electrical charge also changes in the same manner. The various values of the sum $v_0 + v_1$ are very exactly related to each other in the ratio of simple whole numbers. The relation of these numbers gives, directly from Eq. (257c), the relation between the charges which the particle possessed at different times. *Each of the values thus represents a whole number times a definite elementary charge.* Under the assumption that the

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[1] *Phys. Rev.*, **32**, 349 (1911).

TABLE 68.—THE VELOCITY OF A LIQUID PARTICLE WITH VARIOUS CHARGES IN AN ELECTRIC FIELD

V_0	V_1	$V_0 + V_1$ obs.	n	$V_0 + V_1$ calc
0.01078	0.0497	0.0605	2	0.0600
0.01076	0.1095	0.1213	4	0.1200
0.01075	0.0790	0.0898	3	0.0900
0.01085	0.0799	0.0907	3	0.0900
0.01084	0.0493	0.0601	2	0.0600
0.01088	0.0193	0.0301	1	0.0300
0.01085	0.0490	0.0598	2	0.0600
. .	0.0785	0.0893	3	0.0900
0.01084	0.0785	0.0893	3	0.0900
.	0.0790	0.0898	3	0.0900
0.01084	0.0191	0.0299	1	0.0300
0.01088	0.0192	0.0300	1	0.0300
.	0.0493	0.0601	2	0.0600

smallest velocity contained in Table 68 corresponds to exactly one elementary charge, the number of such charges which the particle carried may be calculated very easily, and this number is given in column 4. To illustrate the accuracy of the observations, the sum $V_0 + V_1$ was calculated for each individual observation from the average value of *one* charge $\left(0.0300\ \frac{cm.}{sec}\right)$ and the value of n corresponding to the observation; the results are given in column 5

It should be emphasized once more that these observations involved very little in the way of hypothesis and that, therefore, the existence of an elementary electrical charge of an absolutely definite amount follows from them with absolute certainty

The calculation of the absolute value of e_0 or e_x is more difficult than the qualitative proof of the step-like variation of the charge on the particles, since, in order to obtain it according to Eq. (257*b*), the mass m must be known. This value may be found if we set $m = \frac{4\pi}{3}a^3\delta$ and then substitute the special form of Stoke's law valid for spheres in place of the general equation for the motion of a particle (Eq. (257)). The frictional force f is given by $6\pi a\eta$, where a is the radius of the particle, and η the coefficient of friction. By means of the equation

$$mg = \frac{4\pi}{3}a^3\delta g = 6\pi\eta a \mathrm{v}_0$$

from the velocity of falling v_0, first a is obtained and then the value of m, which can be used in Eq. (257*b*).

But it must now be mentioned that Stoke's law, upon which the calculation of m depends, is not absolutely accurate for very small particles suspended in a gas; the deviations from the law become greater as the gas pressure and the radius of the particles decrease. By systematically varying both quantities (extrapolation of the results from high gas pressure and large particles), Millikan succeeded in eliminating this source of error to a large extent. The final results are

$$e_0 = 4.774 \cdot 10^{-10}\ abs.\ e.s\ u. = 1.591 \cdot 10^{-20}\ abs\ e\ m.u$$

Since all the magnitudes concerned in the calculation of the mass were most carefully determined, the probable error in this number, according to one of the last publications by Millikan,[1] is only about one part per thousand. By applying Eq. (256) he obtained for the Avogadro number

$$\mathbf{N} = 6\ 06 \cdot 10^{23},$$

a number which is considerably more accurate than the results obtained by any other method.[2] In these investigations the charge of electricity was always bound up with matter (ions, cloud droplets, etc.) and positive and negative electricity were exactly the same. As will be shown in the following, *there is a fundamental difference between these two forms of electricity.*

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[1] *Phil. Mag.*, **34**, 1 (1917).

[2] Among others, Ehrenhaft (*Physik. Zeit.*, **18**, 352 (1917)) has made observations similar to those of Millikan, but upon very much smaller particles. He found that the electrical charge was frequently considerably less than the elementary charge established by Millikan Since this result disagrees with all other experience, it does not seem justifiable to lay much stress on it until all possibility of explaining it as being only *apparently* below the normal value is removed. Regener (*Preuss. Akad. Wiss. Ber.*, 632 (1920) showed that very small particles, probably due to a layer of adsorbed gas, had a greater diameter and, therefore, a smaller mean density than was formerly assumed. Other possible ways of explaining Ehrenhaft's results are discussed by R. Bar (*Ann. Physik.*, **67**, 157 (1922)).

Positive electricity is always associated with a material mass which is never smaller than the hydrogen nucleus. Negative electricity often occurs attached to a real or apparent mass which is only about $\frac{1}{1850}$ of that of the hydrogen atom.

c RADIOACTIVE DISINTEGRATION OF ATOMS[1]

269. Fundamental Phenomena of Radioactivity.—In spite of all the experimental and theoretical work, the investigation of the internal structure of atoms would scarcely have lost its hypothetical character at the present time if nature had not presented elements which spontaneously change into other elements, and thus throw out a fraction of the atom. By means of this phenomenon, which is called **radioactivity,** it was possible to gain a real insight into the interior of atoms.

Radioactivity was discovered in 1896 by H. Becquerel in the element uranium, which Klaproth had found in 1789. The discovery of a number of other, previously unknown, radioactive materials, first polonium and later radium (M. and Mme. Curie, 1898), was soon added to this. Besides uranium, other well-known chemical elements, *e.g.*, potassium and rubidium, were shown to be slightly radioactive. Up to 1920, altogether about forty different radioactive substances were known (*cf.* **271**).

This new field was developed, from all sides, most intensively, experimentally and theoretically so that the radioactive research soon reached a certain stopping point, but it must be understood that this did not mean that the final solution of the problem had been reached.

The fundamental fact previously acquired, that a radioactive process involves a transformation of one chemical element into another, was not appreciated at first. In 1902, Rutherford and Soddy first announced the **atomic disintegration theory** developed from the mass of unexplained facts. The relatively late appreciation of this fundamental phenomenon was mainly due to the fact that the immutability of chemical elements was considered as infallible dogma. Further, since the radioactive substances as they exist in nature generally contain a large number of atomic species unknown at that time, the first researches upon radioactivity were submerged under such a mass of phenomena that the fact of atomic decomposition could not be discovered immediately.

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[1] * For a general survey of the subject see RUTHERFORD, E., "Radioactive Substances and Their Radiations," Cambridge University Press (1913).

The main characteristic of radioactive substances which has led to the discovery of all the phenomena is a peculiar radiation proceeding from them. This radiation may be detected by the blackening of a photographic plate, by the excitation of fluorescence, and by its power to make air electrically conducting (to ionize it). The properties of this radiation will be considered in detail in the following. At this point it will merely be emphasized that, theoretically, three different kinds of radiation, α, β, and γ, are to be distinguished. Since the γ-radiation never occurs by itself, but always together with a β-radiation or (somewhat less in intensity) with an α-radiation, it can be looked upon as a secondary effect, which in the following will not be especially considered.

The simplest means of distinguishing between α- and β-rays is that the α-rays are very much more easily absorbed than the β-rays. The α- and the β-rays sent out by different radioactive substances are not alike. Experimentally, the differences between the α-rays of the various elements are most readily established by their range in air (at atmospheric pressure and 15°C.). The β-rays are best distinguished through their absorption powers in aluminium. In the latter case we determine either the so-called "*Halbierungsdicke*" (the thickness of aluminium which reduces the intensity of the beam by one-half) or the **absorption coefficient** $\left(\text{the reciprocal of the length of the path which reduces the intensity to } \frac{1}{e} \text{ of its original value}\right)$.

Corresponding to each radioactive transformation there is a definite radiation peculiar to it alone,[1] so that the existence of a definite radioactive substance can be proved by the characteristic radiation involved in its decomposition. For example, radium in its decomposition sends out α-rays with a range of 4.75 *cm.;* uranium I of only 2.50 *cm.;* while the decomposition of uranium X_1 involves a β-radiation with a "Halbierungsdicke" of $1.5 \cdot 10^{-3}$. A minute quantity of material, which would be insufficient for a chemical test, suffices for the detection of a highly radioactive (*i e* , rapidly decomposing) substance by means of the radioactive radiation.

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[1] This fact was clearly recognized only after a relatively long time (see HAHN, OTTO and MEITNER, L., *Physik. Zeit.*, **10**, 697, 741 (1909)). Moreover, this does not exclude the possibility of a single radioactive element changing simultaneously partly into one and partly into another atomic species. In this case two kinds of radiation are sent out (see Table 69).

270. The Rate of Disintegration of an Atomic Species. The Radioactive Disintegration Constant.—If a single radioactive substance be isolated, it is found that the characteristic radiation sent out from it diminishes with time, and Eq. (27*b*) (disintegration curve), already derived in **13**, is found to be exactly confirmed by experiment. Therefore, the original statement (Eq (17)) must be considered as correct or, expressed in words, that *in a definite time (e g , 1 sec) an absolutely definite fraction of the total number of atoms always disintegrates.*

If, however, only a small number of radioactive atoms can be observed, it is certainly not to be expected that this fraction is exactly constant at every moment; certain irregular fluctuations must occur. This phenomenon is completely explained by the assumption that *the individual atoms disintegrate explosively quite independent of each other.* It is then conceivable that such purely accidental explosions will occur more frequently during some time intervals than others.[1] The fluctuations are obliterated only when a large number of atoms are observed at one time; only then is it possible to obtain a continuous disintegration curve. Disregarding the fluctuations of this curve, the fraction of the substance which disintegrates in unit time (this was indicated in Eq (17) by k and was called the **disintegration or radioative constant**) represents an invariable quantity[2] for each atomic species, and is another means of distinguishing between the various radioactive substances. In place of the radioactive constant, its reciprocal value, the **average life**, or the **half-life period** which is only 0.693 . . . × *the average life* (*cf.* **13**), is generally used.

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[1] Even the decomposition of a *single* atom can be experimentally demonstrated with some degree of certainty in various ways by means of the radiation emitted (see **367**).

[2] If it is desired to make the radioactive constant, and thus the fraction of the atoms actually decomposing, independent (in an abstract sense) of the fluctuations in the disintegration curve, it must be defined as the *probability* for the decomposition of any one atom in unit time.

The radioactive constant or average life of an atomic species is always the same no matter what it may be combined with chemically. It may also be mentioned that a chemical interference during the transformation does not have the slightest influence on the disintegration curve. It follows from this that *the radioactive properties are completely independent of the way in which the atoms are linked together.*

It is especially striking that the radioactive constant, contrary to the chemical velocity of reaction, is not in the least influenced by the temperature. Of course, experiments can be performed only up to a temperature of about 1000°, and it is very probable that the temperatures which exist in the hottest stars and nebulae may yet influence the radioactive process.

With regard to what has already been said about ideal solid bodies (see **58**), it may be added that the ideal limiting condition for such bodies, which is independent of temperature and which molecularly built matter first attains just above the absolute zero, may be reached even at 1000° for atoms with respect to their radioactive behavior—therefore that even a temperature of 1000° represents an "immediate vicinity" to the absolute zero in this case.

271. The Radioactive Families of Elements. The Displacement Law.- Neglecting the slightly radioactive elements potassium and rubidium, which have not as yet been completely investigated with respect to their transformation products, radioactivity becomes practically limited to a number of elements with atomic weights greater than 200.

This fact indicates a certain instability in the heaviest atoms which increases with the atomic weight, even though the instability does not increase regularly. It also suggests the reason why atoms of considerably higher atomic weight than that of uranium are not capable of existence, but, of course, it does not exclude the possibility of elements of higher atomic weight than that of uranium in the hottest fixed stars. However, such elements, because of their strong radioactivity, must have decomposed long ago during the cooling of the solar system and the earth.

TABLE 69.—RADIOACTIVE SUBSTANCES AND THEIR TRANSFORMATIONS[1]

Group in periodic table	Uranium series				Thorium series	
VI	U I	4.67 × 10^9 a				
	↓ α					
IV	U X_1	24.6 d				
	↓ β					
V	U X_2	1.15 m				
	↓ β(γ)					
VI	U II 3%	2 × 10^6 a				
	97% ↓ α		↘			
IV	Io	6.9 × 10^4 a	U Y	1.04 d	Th	1.31 × 10^{10} a
	↓ α		↓ β		↓ α	
II	Ra	1690 a			Ms Th_1	6.7 a
	↓ α (β + γ)		↓		↓ β(?)	
V			Pa	1.2 × 10^4 a		
			↓ α		↓	
III			Ac	20 a	Ms Th_2	6.2 h
			↓ β		↓ β and γ	
IV			Rd Ac	19.5 d	Rd Th	2.02 a
			↓ α(β)		↓ α(β)	
II			Ac X	11.4 d	Th X	3.64 d
	↓		↓ α		↓ α	
0	Rn	3.85 d	An	3.9 s	Tn	54 s
	↓ α		↓ α		↓ α	
VI	Ra A	3.0 m	Ac A	2.0 × 10^{-3} s	Th A	0.14 s
	↓ α		↓ α		↓ α	
IV	Ra B	26.8 m	Ac B	36.1 m	Th B	10.6 h
	↓ β(γ)		↓ β and γ		↓ β and γ	
V	Ra C 0.03%	19.5 m	Ac C	2.15 m	Th C 35%	60 m
	99.97% ↓ β ↘ α		↓ β ↘ α		65% ↓ β ↘ α	
VI	Ra C′	10^{-6} s	Ac C′	approx. 5 × 10^{-3} s	Th C′	10^{-11} s
III	↓ α Ra C″	1.4 m	↓ α Ac C″	4.71 m	↓ α Th C″	3.1 m
	↓ ↙ β		↓ ↙ β and γ		↓ ↙ β and γ	
IV	Ra D	16.5 a	Ac D or Ω (Pb) 206 Actinium lead	∞	Th D or Ω (Pb) 208 Thorium lead	∞
	↓ β and γ					
V	Ra E	5.0 d				
	↓ β					
VI	Ra F (Po)	136 d				
	↓ α					
IV	Ra G or Ω (Pb) 206 Uranium lead	∞				

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[1] The data and nomenclature in this table have been brought into general agreement with the Report of the Committee on Chemical Elements, *J. Am. Chem. Soc.*, **45**, 870 (1923). Confirmatory evidence on the transformations below AcC seem to be desirable.

The origin of all radioactive substances (with the exception of K and Rb) may be traced back to two elements, uranium and thorium, *i e*, as far as it can now be determined, there are two radioactive families which are independent of each other

A survey over the two radioactive families and the relations of their independent members is offered in Table 69 From this is to be observed: (1) the group of the periodic system to which atomic species belongs, (2) the half-life period of each atomic species, (*a*) years, (*d*) days, (*h*) hours, (*m*) minutes, (*s*) seconds, (3) whether the transformation follows from the emission of α- or β-rays (these are called α- or β-transformations)

It appears that, not far from its origin, the uranium family divides into two branches,[1] which, after a certain point, show a striking parallelism with a portion of the thorium family. Counting from the gaseous emanations, radon, actinon, and thoron, all three series divide again at the third new atom, RaC′, AcC′, ThC′, and each at first forms two different products (RaC″, RaC‴, etc), of which one is exceedingly unstable, the half-life period of ThC″ is 10^{-11}s! Yet further along in the transformation process a single product (RaD, etc) is formed from both branch products The most important result indicated in Table 69 is the **radioactive displacement law,** first announced by Soddy and by Fajans in 1913 [2] According to this law, the chemical properties are changed in an entirely definite manner in each α- or β-transformation *An α-transformation moves the atom two columns to the left in the periodic system (smaller positive valence). A β-transformation moves it one column to the right (higher positive valence)* The transformation from one series of the periodic system to the next higher thus makes it possible to place the chemically inert gaseous elements (Rn, An, Tn) either in Group O or in Group VIII.

272. Stationary Radioactive Equilibrium between Different Substances.—As soon as a radioactive atomic species has been formed from its parent substance, it begins to transform into the next following species of the family. If a preparation which had been made a long time previously or if a natural uranium or thorium mineral is observed, a large number of different radioactive substances will be found existing simultaneously. Each radioactive substance will, in the course of time, reach a stationary state such that in unit time the amount forming will be the same as the amount decomposing. The more unstable an atomic species, the more rapidly it decomposes, the less possible it becomes to concentrate it, and, therefore, the smaller the amount of it apparently contained in the substance under examination.

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[1] The exact point where the branching takes place is not yet quite certain.

[2] When this law was first discovered, Table 69 had a relatively large number of gaps, the displacement law was of great assistance in its completion.

If Eq (17) is applied once to the parent substance and then again to the product of its transformation, we get

$$dx_0 = -k_0x_0dt.$$
$$dx_1 = -k_1x_1dt.$$

Now dx_0, the number of transformed atoms of the parent substance in the stationary state, must always equal dx_1, the number of atoms of its transformation product, since the latter must otherwise either increase or decrease. We, therefore, obtain the relations

$$\frac{k_0}{k_1} = \frac{x_1}{x_0} \quad \text{or} \quad \frac{\tau_0}{\tau_1} = \frac{x_0}{x_1}$$

or, in words, in the stationary state the amounts of the atomic species are proportional to their half-life periods τ. If the half-life period of the one atomic species is known, it is only necessary to determine the amounts of the two existing atomic species in order to calculate the half-life period of the other species. This method for the determination of the half-life period may be applied to minerals, since the age of their existence guarantees that the stationary state has been reached. It also gives a welcome supplement to the method of the disintegration curve for those atomic species which decompose very slowly. For example, the half-life period of uranium can be determined in this way from the knowledge of the half-life period of radium and the ratio of the amounts of radium and uranium found in a uranium mineral.

273. Atomic Weight of Radioactive Atomic Species.—It has already been emphasized that, in their half-life periods and in the radiation sent out during their transformation, the radioactive elements possess properties which are strictly characteristic for each atomic species and which, therefore, serve for their indentification and mutual differentiation.

To these properties in most cases the atomic weight must also be added. This, however, can be directly established only by much tedious work if the usual chemical methods are applied. From the nature of the α-rays it is seen (*cf.* **280**) that every α-transformation must involve a decrease of four units in the atomic weight, while a β-transformation cannot perceptibly change this constant. Thus the atomic weight of each member of the series

TABLE 70.—ATOMIC WEIGHTS OF THE RADIOACTIVE SPECIES
In round numbers

At wt	0 or VIII	I	II	III	IV	V	VI	VII
197		**Au**						
200			**Hg**					
204				**Tl**				
206				βAcC″	RaG, AcD			
207					**Pb**			
208				βThC″	**ThD**	**Bi**		
210				βRaC″	βRaD, βAcB	βRaE, αβAcC	**αPo**, α AcC′	
212					βThB	α β Th C	αThC″	
214					βRaB	α β Ra C	αRaC″, αAcA	
216							αThA	
218	αAn						αRaA	
220	αTn							
222	**αRn**		αAcX					
224			αThX					
226			**αRa**	**βAc**	αRaAc			
228			βMsTh$_1$	βMsTh$_2$	αRaTh			
230					αIo, βUY	**αPa**		
232					**αTh**			
234					βUX$_1$	βUX$_2$	ααU$_{II}$	
238							**αU$_I$**	

in a radioactive family can be found if that of the initial substance or any other member of the series is known Accepting the atomic weight of uranium I as 238 (in round numbers) and that of thorium as 232, then the atomic weights of the remaining atomic species follow in the manner indicated in Table 70. *It appears that a number of different radioactive atomic species possess the same or very nearly the same atomic weight and, therefore, that the atomic weight is a very much less characteristic property than the radioactive properties.*

274. Peripheral Properties of Radioactive Elements.—A number of radioactive elements behave very peculiarly with respect to their chemical properties. *In spite of the above mentioned, strictly characteristic, radioactive properties and many differences in atomic weight, a number of these radioactive substances cannot be separated from each other by any chemical method.*[1]

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[1] This statement was made at nearly the same time (1909-10) by several investigators (Soddy, Stromholm and Svedberg, Marckwald) and with special emphasis by SODDY in his "Chemistry of the Radioactive Elements," Longmans, Green & Co (1911), new ed. (1914).

As an example we may cite the attempts of Keetmann[1] to separate ionium and thorium, which gave negative results, in spite of the greatest care and numerous repetitions. Just as little success was met with in attempts to separate mesothorium I from radium (Soddy, 1911), radiothorium from thorium, uranium I from uranium II, etc (the radioactive elements of short-life period were less suitable for the purpose of chemical separation). The final products of radioactive transformation (RaG, AcD, ThD) are especially suitable for the comparison of the chemical properties It was found that, from a chemical viewpoint, it was not only impossible to differentiate them among themselves, but that there was no difference between them and ordinary lead. An identification of RaG or AcD, which without doubt exist in perceptible amounts in uranium minerals, is not possible by radioactive properties, since they are inactive, but, according to Table 70, it is to be expected that they possesses an atomic weight approximately one unit lower than ordinary lead. Honigschmidt and Horovitz as well as T. W Richards and Wadsworth[1] succeeded in demonstrating that the "lead" always found in very pure uranium minerals possessed an atomic weight which was very nearly 206, which differs by more than one unit from the usual lead (207 16). The "lead" from uranium minerals is thus not identical with ordinary lead, but is to be designated as RaG (with some AcD), although not the slightest chemical difference between them can be shown.

In the same way Honigschmidt showed that the "lead" from a pure thorium mineral had an atomic weight that was only a little smaller than the value 208 required for thorium D.

The chemically inseparable radioactive elements were then, as far as possible, compared with each other by means of several other characteristic physical properties. The visible spectrum was examined with special care.

In the earlier researches (Exner and Haschek, 1912–15), in which ionium was compared with thorium, and lead with radium G, no difference in the spectra could be shown. In these investigations the accuracy attained in measuring the wave length was 0.2 Å. Only after the accuracy of measurement had been increased to about 0.001 Å. by means of an interference method was it possible to demonstrate differences between the lines of RaD, ThD, and ordinary lead, which were of the order 0.002 to 0.005 Å. (*Aronberg, 1917; Merton, 1919). This difference is very slight in comparison with the very large differences in the spectra of chemically dissimilar atoms and it will be neglected in the following discussion, even though it is a matter of considerable theoretical importance.[1]

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[1] *Jahrb Radioakt Elektronik*, **6**, 265 (1909)

[1] * *J. Am Chem. Soc*, **38**, 2613 (1916). Further references will be found in this article.

It can also be shown that the elements in question are identical (within experimental error) with respect to melting point, molecular solubility, volatility, electrochemical potential, magnetic properties, and atomic volume in the solid state.[2]

Since, according to **264**, the origin of these properties, and especially the chemical properties, is to be sought for in the periphery of the atom, the following conclusions are reached:

1. *The chemically inseparable elements must have the same constitution in the peripheral part of the atoms*, but at the same time the portion in which the radioactive properties are localized must be different. The latter, as distinguished from the periphery, is called the atomic nucleus.

2. Since the weight of an atom does not appear to be directly connected with its peripheral properties (there are radioactive elements with the same atomic weights and different chemical properties, **isobars**, as well as different atomic weights and the same chemical properties, **isotopes**), it is not very difficult to suppose that *the mass of the atom is not concentrated in the periphery, but in the nucleus*. This conception will be completely established later by direct arguments

275. The Arrangement of the Radioactive Elements in the Periodic System.—The traditional idea of the chemical element was very much shaken by the discovery of the radioactive transformation of atoms and the Rutherford atomic decomposition theory The older conceptions, which defined a chemical element as a fundamental substance which could not be further decomposed by the use of the methods of experimental chemistry, could no longer be upheld except in a formal sense. But besides this, a radioactive decomposition took place spontaneously, and could not, at least experimentally, be influenced by chemical means The older conception of a chemical element also insisted upon the properties of immutability and permanent stability, which henceforth had to be abandoned.

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[1] * For further discussion see Aston, "Isotopes," 123, Arnold, London (1923); Das, P., *Chem. Abstracts*, **18**, 2281 (1924).

[2] See also Fajans, K., "Radioactivity and the Latest Developments in the Study of Chemical Elements," translated by Wheeler and King, E. P. Dutton & Company (1924). Also Hevesy and Paneth, "Lehrbuch der Radioaktivitat," Leipzig (1923).

A difficult problem arose when the attempt was made to classify and to arrange in the periodic system of elements these newly discovered elements which differed in their radioactive properties and very often also in their atomic weights. There soon proved to be no place for them—at least, not if it was attempted to arrange them in the usual way in which each element was to be assigned to a special place.

The proposal was then made that, even in spite of their different atomic weights, all chemically inseparable elements should be assigned to a common place in the periodic table like a single element (Stromholm and Svedberg, Soddy, 1909) and the same atomic number (Soddy, Bohr, 1913). The elements thus belonging together were designated by Soddy as **isotopes** (ἴσος = the same, τόπος = place) and according to Paneth are to be considered as one and the same chemical element. Under the present, quite generally accepted views, we have as the only remaining, distinguishing characteristic of a chemical element the identity of all peripheral, especially the chemical, properties of the atoms, while the stability of the atoms, their other radioactive properties, and, in particular, the atomic weight are without significance *A chemical element is henceforth to be defined as a chemically[1] undecomposable substance which, within very narrow limits, possesses definite peripheral properties.*

276. The Resolution of Non-radioactive Elements into Isotopic Species.—In the creation of the concept of "isotopes," Soddy expressed the supposition that the occurrence of isotopes is not confined to the radioactive elements, but that even ordinary elements might also have isotopic varieties with different atomic weights. Accordingly, a chemical element could consist of a mixture of different isotopes. It is clear that such a "mixed element," depending upon the proportions of the various isotopes contained in it, might not have a whole number for its atomic weight even though the atomic weights of the individual isotopes were exactly whole numbers. This offers the possibility of retaining the principle of Prout's old hypothesis, and to explain the deviations from the whole-number rule among the elements in a simple way. An experimental decision on the question whether the ordinary non-radioactive elements consist of definite mixtures of isotopes (the mixed elements) involved extraordinary difficulties, owing to the similarity of every one of the properties which could be used for the separation of the different substances.[1] The atomic weight, which was the only measurable magnitude, formed the basis for the methods of separating isotopes The following possibilities appeared:

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[1] Yet, by means of very powerful *physical* influences under certain circumstances, it is possible to effect a decomposition according to recent investigations by Rutherford (see **293**).

1 According to the law of energy partition, the velocities of gaseous atoms of different atomic weights must be different. The methods[2] previously mentioned for the direct measurement of the molecular velocities of *single* molecules are not at present sufficiently exact to carry out a separation of isotopic species It was, therefore, necessary to use phenomena based upon the average molecular velocity of a large number of molecules For example, the velocity of diffusion of a gas and of flow through narrow pores depends directly upon the molecular velocity

Attempts to separate the isotopes of an element on the basis of the difference between their average molecular velocity have recently been made by a number of investigators using various modes of attack, and so far have led to the result that an appreciable change in the ratio of the mixture could be obtained, but of course the isotopes could not be completely separated. Harkins[3] succeeded in resolving ordinary chlorine into two fractions with somewhat different (average) atomic weights, by repeatedly

[1] * For a review of the various methods which have been applied to this problem, see chap XI of F W. ASTON's monograph, "Isotopes"

[2] For examples see STERN, O, *Z Physik*, **2**, 49 (1920)

[3] *Nature*, **105**, 230 (1920), * HARKINS and HAYES, *J Am Chem. Soc.*, **43**, 1803 (1921), MULLIKAN and HARKINS, *ibid.*, **44**, 37 (1922).

filtering through clay tubes. Brönsted and v. Hevesy[1] allowed mercury to distill under very low pressure,[2] and likewise obtained two fractions which could be distinguished by their measurably different densities.

2. By the method of deflecting the positive rays[3] it was possible to measure the mass of single atoms very exactly, and in this way to establish the presence or absence of the various isotopes. This method in its simplest form is described briefly in **279.** Aston,[4] by applying certain important improvements, increased the accuracy to the point where it is now possible to find the atomic weight of individual atoms with an accuracy of about 0.1 per cent. In the same way, Dempster[5] (with an experimental arrangement somewhat different from Aston's) succeeded in resolving the isotopes of several non-radioactive elements.

The investigations performed by Aston on a large number of elements gave a remarkable confirmation of the hypothesis of "mixed elements." The numbers found for the elements investigated up to the present time are summarized in Table 71. The main result expressed in this table is that a portion of the elements really do consist of different isotopes, and that the atomic weights of all the individual isotopes of which the elements are composed are *exactly whole numbers.* Strange to say, only hydrogen, with an atomic weight of 1.008, forms an exception.[6]

[1] *Nature* (Sept 30, 1920); *Phil Mag*, **43**, 31 (1922)

[2] In this case the rate of evaporation is directly proportional to the average molecular velocity (see **135**) or, since the quantity $\frac{MV^2}{2}$ must be constant, it must be inversely proportional to the square root of the molecular weight This is also expressed in Eq (135), since $B \sim \frac{1}{\sqrt{M}}$.

[3] *THOMSON, J J, *Phil Mag* (6), **13**, 561 (1907); also footnote to **279.**

[4] *Phil Mag*, **39**, 449, 611; **40**, 628 (1920) See also ASTON's monograph, "Isotopes"

[5] *Phys Rev* (2), **11**, 316 (1918); **17**, 427 (1921); **20**, 631 (1922)

[6] By means of an especially sensitive differential method, Aston has recently been able to demonstrate that the atomic weights of several of the heavier elements also differ from those of their neighboring elements by amounts which are not exactly whole numbers.

On the basis of the principle of the equivalence of energy and mass (see **259**), this last result may be considered to signify that the combination of a number of H atoms to form a heavier atom represents a strongly exothermic reaction. For example, if calculated according to the Eq. (254), the forma-

TABLE 71.—ISOTOPES OF NON-RADIOACTIVE ELEMENTS[1]

Element	Mean atomic weight	Atomic weights of the isotopes in the order of their frequency of occurrence	Element	Mean atomic weight	Atomic weights of the isotopes in the order of their frequency of occurrence
H	1.008	1.008	Ni	58.68	58, 60
He	4.00	4	Zn	65.37	64, 66, 68, 70
Li	6.94	7, 6	As	74.96	75
Be	9.02	9	Se	79.2	80, 78, 76, 82, 77, 74
B	10.82	11, 10	Br	79.92	79, 81
C	12.00	12	Kr	82.92	84, 86, 82, 83, 80, 78
N	14.01	14	Rb	85.5	85, 87
O	16.00	16	Sr	87.63	86, 88
F	19.00	19	Zr	90.6	89.9, 91.9, 93.9, (95.9)
Ne	20.2	20, 22	Sn	118.70	120, 118, 116, 124, 119, 117, 122, (121)
Na	23.0	23	Sb	121.77	121, 123
Mg	24.32	24, 25, 26	I	126.92	127
Al	27.1	27	X	130.2	129, 132, 131, 134, 136, 128, 130, (126), (124)
Si	28.3	28, 29, 30	Cs	132.81	133
P	31.04	31	Ba	137.37	138, (136), (137)
S	32.07	32	La	139.0	139
Cl	35.46	35, 37	Ce	140.25	140, 142
Ar	39.9	40, 36	Pr	140.9	141
K	39.1	39, 41	Nd	144.3	142, 144, 146, (145)
Ca	40.7	40, 44	Er	167.7	164–176 (impure sample)
Fe	55.84	56, 54	Hg	200.6	202, 204, 197, 198, 199, 200

[1] ASTON, *Phil. Mag.* (May, 1923) and **Nature*, **113**, 856 (1924), **114**, 273 (1924).

d. THE CORPUSCULAR RAYS

277. Corpuscular Nature of α- and β-rays.—It has already been mentioned that every radioactive transformation is accompanied by the emission of a characteristic α- or β-radiation, the nature of which must now be briefly discussed.

The investigations of C. T. R. Wilson (1911–13)[1] indicate very plainly the nature of these rays. The methods used depended upon the fact that these rays ionize gases. The ions in the gas

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tion of a He atom involves a molecular heat of reaction equal to $4 \times 0.008 \times 9 \times 10^{20} \simeq 3 \times 10^{19}$ *ergs*, which is many times greater than the heat given out by radioactive transformations (**282**).

[1] **Proc. Roy. Soc.*, **87**, 277 (1912). More recent work has been done by SHIMIZU, *ibid.*, **99**, 425, 432 (1921) and by BLACKETT, *ibid.*, **102**, 294 (1922); **103**, 62 (1923).

form condensation centers for supersaturated water vapor (R. v. Helmholtz, 1887), *i.e.*, a fog droplet forms about each gas ion in supersaturated water vapor. Under sufficiently strong illumination these droplets can be made visible and, by means of instantaneous photographs, the positions and the density of the gaseous ions resulting from the radiation can be directly determined. Figures 58 and 59 give reproductions of some of Wilson's photographs.

They show that the gaseous ions from both α- and β-rays are formed along separate and very definite paths (for the β-rays this is less clear).

The α- and β-rays, therefore, do not consist of a wave motion like ordinary light and X-rays, but must be of a corpuscular nature; *they may be considered as particles thrown off by radioactive atoms during their disintegration and, therefore, represent cleavage products of decomposing atoms.*

278. The Deflection of Corpuscular Rays by Electric and Magnetic Fields.—If a narrow beam of α- or β-rays is passed between two poles of a magnet or two plates carrying opposite electric charges, it will be deflected. From this it may be concluded qualitatively that the particles carry electric charges. The charge on the particle may be directly demonstrated if a metal plate is put in the path of the ray; it can soon be ascertained that the plate has become charged

For a quantitative treatment let the particle have a mass m and a charge e If an electric field or potential gradient $X = \frac{dE}{dx}$ acts on it in the direction of its original motion (x-axis), it will be either accelerated or retarded, and according to Eq. (13) and **21** we have

$$mg' = m\frac{dv}{dt} = \mathfrak{K} = \frac{dE}{dx}e$$

or since

$$\frac{dx}{dt} = v,$$

$$m\,v\,dv = \frac{m}{2}d(v^2) = e\,dE,$$

from which it follows that

$$\frac{m}{2}(v^2 - v_0^2) = Ee \qquad (258)$$

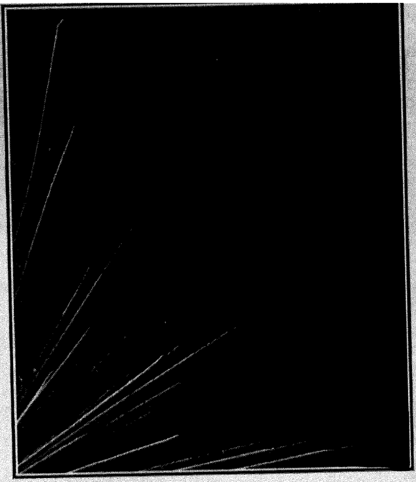

FIG. 58.

FIG. 59.

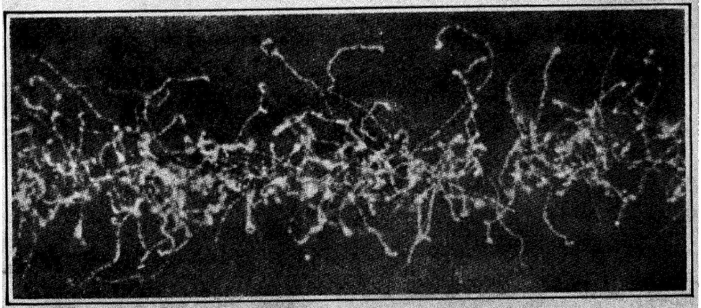

FIG. 62.

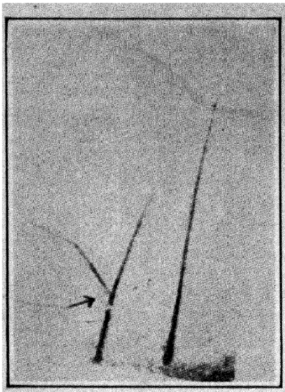

Fig. 64.

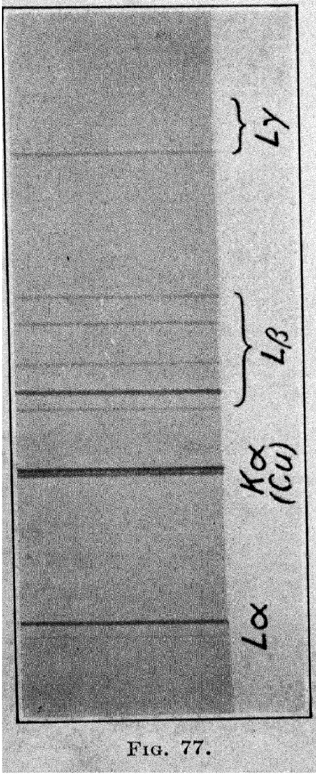

Fig. 77.

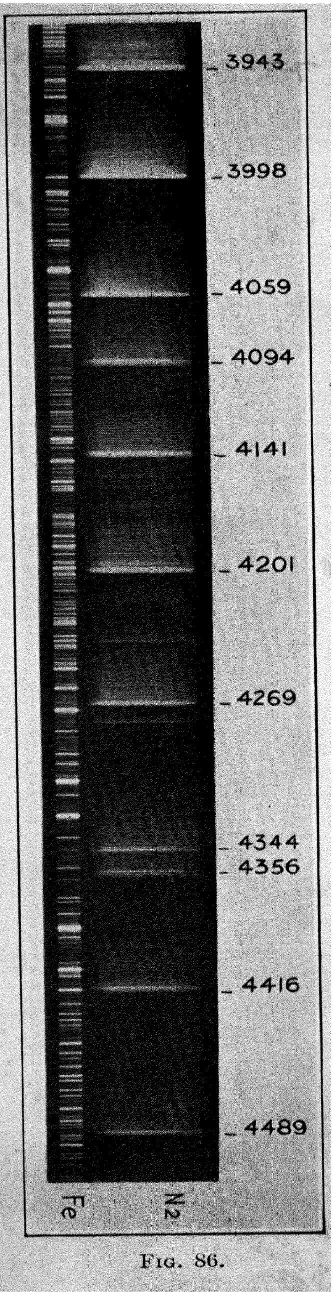

Fig. 86.

if $V - V_0$ represents the change of velocity of the particle while passing through a potential difference E. Moreover, Eq. (258) follows directly from the energy principle, since it states that the increase or the decrease of the kinetic energy of the particle is equal to the work performed by the electric field. If V_0 is vanishingly small, Eq. (258) simplifies to

$$\tfrac{1}{2}mV_0^2 = Ee,$$

and the velocity of the particle is given by

$$V = \sqrt{2E\frac{e}{m}}. \tag{258a}$$

If the electric field is placed at right angles (y-axis) to the original path of the particle, then the particle will describe a parabola exactly as a projectile under the influence of gravity. After a time t the particle has traveled along the x-axis a distance $x = V_0t$ and along the y-axis

$$y = g'\frac{t^2}{2} = \frac{e}{2m}\frac{dE}{dy}t^2$$

or

$$y = \left(\frac{e}{2mV_0^2}\frac{dE}{dy}\right)x^2 = \left(\frac{e}{2mV_0^2}X\right)x^2. \tag{259}$$

From the dimensions of the deflection parabola, one of the factors (say V_0) contained in the parentheses can be calculated, if the others are known.

A magnetic field placed perpendicular to the direction of motion of the particle exerts a force on the latter which acts perpendicular to the field as well as perpendicular to the motion of the particle at any moment. We must now bring into the calculation the fundamental law of electrodynamics which states that a conductor through which a galvanic current is flowing, placed in a magnetic field perpendicular to it, is affected by a force which is perpendicular to both directions. The magnitude of this force is $\mathfrak{K} = Hi\Delta x$, where H is the strength of the magnetic field, i is the strength of the current, and Δx the length of the conductor. In place of the expression $i\Delta x$, we have the quantity $eV_0 = e\frac{\Delta x}{\Delta t}$ for the corpuscular rays, since the current strength i is defined by $\frac{e}{\Delta t}$, *i.e.*, the amount of current flowing through the cross-section of the conductor in unit time.

Now the centrifugal force $\frac{mV_0^2}{r}$ acts in opposition to the force which tends to deflect the particle from its path. Therefore, an equilibrium must be established, in which the deflecting force is just equal to the centrifugal force, so that

$$\frac{mV_0^2}{r} = eV_0H \quad \text{or} \quad Hr = \frac{mV_0}{e}. \tag{260}$$

If V_0 is known, then the ratio[1] $\frac{e}{m}$ can be calculated from the measurements of the radius r of the circle described by the particle and the H of the magnetic field, and conversely. By combining the methods of electric and magnetic deflection it is possible to determine both V_0 and $\frac{e}{m}$ The equations are then

$$V_0 = \frac{Xx^2}{2Hyr} \tag{261}$$

$$\frac{e}{m} = \frac{Xx^2}{2H^2yr^2}. \tag{262}$$

These Eqs. (261 and 262), of course, hold rigorously only if the velocity of the particle is small compared with that of light. If the velocity V is comparable to the velocity of light V_l (which is certainly the case with the β-rays), then the mass m can no longer be regarded as constant, but will be function of the velocity. The phenomenon is a necessary consequence of *Einstein's special relativity principle*, which requires an apparent increase of mass $m-m_0$, and for which the following expression must hold

$$m = \frac{m_0}{\sqrt{1 - \frac{V^2}{V_l^2}}} \tag{263}$$

Investigations on rapidly moving particles have also established this equation.

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[1] The ratio $\frac{e}{m}$ is usually called the "specific charge" of the particle, since it represents the charge carried by a unit mass of particle.

279. Deflection of Positive Rays.[1]—Equations (261) and (262) may first be applied to a sort of artificial corpuscular rays which are not of a radioactive nature, and which find application in the methods (see **276**) used by Thomson, Aston, and Dempster[2] for determining the masses of isotopic atoms. According to a method discovered by Goldstein, a corpuscular ray can theoretically be produced from every gaseous atom or molecule. The substance in the form of an easily vaporized compound is introduced at a very low pressure into the electrical discharge tube A-K (Fig. 60), whose cathode K is a solid metal block with a very small hole bored axially through it When an electric discharge passes through the tube, a portion of the gas becomes positively ionized. The ionized particles move towards the cathode and for the most part are neutralized on its surface. A small fraction, however, which lie directly in the direction of the hole, do not rebound, but pass through it as corpuscular rays traveling along straight lines. By means of an electric field (between L-L) and a magnetic field (the magnet PQ) the rays are deflected and finally reach the photographic plate R, where their point of impact is registered. Since the initial velocities V_0 of the individual, positive particles are very different, the beam will be drawn apart by the magnetic and electric deflections. Therefore, the point of impact with the plate R will not be a

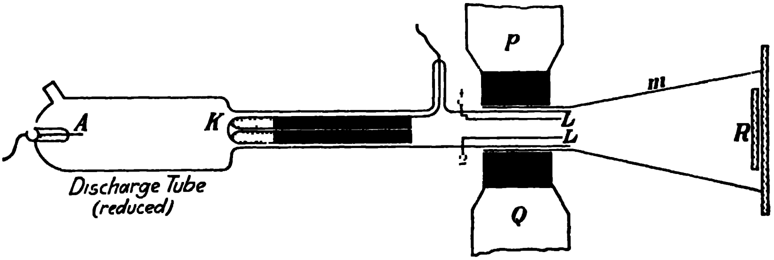

FIG 60

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[1] Goldstein called the hole in the cathode a "canal," hence he named them "Kanalstrahlen" * The English term, following J J Thomson, is **positive ray.** An exhaustive discussion of positive rays, their production, properties, applications, etc is given by THOMSON, J. J. in "Rays of Positive Electricity," Longmans Green & Co (1921).

[2] * DEMPSTER, *Phys Rev.*, **11**, 316 (1918).

single sharp point, but a curve which represents a parabola for each definite value of $\frac{e}{m}\cdot$ This may be shown by a special calculation to be the result of the relation between x and y in Eq. (262) However, by the use of special precautions Aston proved that it was possible to unite at a single point particles with different velocities v_0 but the same ratio $\frac{e}{m}\cdot$ The apparatus became considerably elaborated, but the accuracy of the results was very much increased.

280. Charge, Mass, and Velocities of the α-rays.—The application of the above deflection method to the radioactive corpuscular rays leads to the following results:

The particles of the α-rays are positively charged The ratio $\frac{e}{m}$, according to the most exact investigation, is $4.820 \cdot 10^3$ (*e.m.u.*), while that of a singly charged H atom is $\frac{9650}{1.0077} = 9.573 \cdot 10^3$ *e.m u.*

It may now be shown that each α-particle carries two elementary charges. and therefore its mass must be four times that of the H atom.

The proof of the double charge on the α-particle depends on the simple fact that if the total charge of a definitely known number of particles is measured by bringing them to an electrometer, the charge on the individual particle is the quotient of the number into the total charge. Regener (1909) succeeded in counting the individual α-particles by allowing them to fall upon a thin zinc sulfide or diamond plate. Upon striking the plate the particle produced a very weak but observable (under the microscope) flash of light, which is generally known as the "scintillation phenomenon" Rutherford and Geiger allowed the α particles to enter an ionization chamber where they ionized the enclosed gas. By suitable choice of experimental conditions (production of ionization by impact, *cf.* **287**) the entrance o every α-particle into the ionization chamber was indicated by a perceptible throw on the electrometer connected with the chamber. For the charge of the α-particle obtained by these methods, Regener found $9.56 \cdot 10^{-10}$ and Rutherford and Geige

$9.30 \cdot 10^{-10}$ *e.s.u.*, which is very nearly double the value for the elementary electric charge $4.77 \cdot 10^{-10}$ *e.s.u.* given in **268**.[1]

Since helium is the only element with an atomic weight in the neighborhood of four and, further, since radioactive minerals nearly always contain appreciable amounts of occluded helium, there can scarcely be any doubt that the α-particles are identical with the doubly charged helium atom. This conclusion was finally tested directly by Rutherford and Royds (1909) and established as follows: a radioactive preparation (RaEm), from which α-rays are sent out, was enclosed in a very thin-walled glass tube penetrable by the α-rays; the glass tube was placed in a highly evacuated space in which the presence of helium could be proved after a time by spectral analysis, even though the thin glass tube was impermeable to ordinary helium atoms.

Observations, using the scintillation method, on a weak preparation sending out α-rays demonstrated that the α-particles are always thrown out as single individual particles, and not in pairs or triplets. It follows, therefore, that in its decomposition a radioactive atom always loses only one α-particle (He atom). This is the proof for the above (see **273**) assertion that in a radioactive α-transformation the atomic weight of the transformation product must be four units less than that of the original substance.

The initial velocities of the α-particles sent out by the various radioactive transformations varies between 1.3 and $2.3 \cdot 10^9$ *cm/sec*, or about one-fifteenth to one-twentieth of the velocity of light. The radiation from each kind of α-transformation (*e.g.*, Ra to RaEm, etc. (Table 69)) is homogeneous, *i.e.*, all the α-particles have the same velocity at the time of being thrown out of the atom.

According to an empirical relation given by Geiger, the range R of the α-particle in air depends in a simple manner upon this expulsion velocity. The relation is

$$R = 0.98\, V_0^3 \cdot 10^{-27}\ cm,$$

from which the velocity V_0 can be easily calculated from a given range. Between the decomposition constant k and the range R, Geiger and Nutall have found the empirical relation

$$\log k = A + B \log R,$$

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[1] If the double charge on the particle is considered as established by this comparison, the elementary charge e_0 is found to be 4.78 and $4.65 \cdot 10^{-10}$, which gives 6.05 and $6.22 \cdot 10^{23}$ for the value of Avogradro's number **N**.

in which A and B are constants; A has different values in the different radioactive families, but B is the same for all [1]

That the more rapidly an atom decomposes (*i e.*, the more unstable it is) the greater is the velocity of the expelled product, and therefore the greater must have been the internal energy of the atomic nucleus before the disintegration, is quite in analogy with the somewhat trivial example that the probability that a steam boiler will explode is greater the higher the internal pressure. F. A. Lindemann (*Phil Mag*, **30,** 560 (1915)) gives the theoretical significance of the Geiger-Nutall relation along somewhat different lines

281. Charge, Mass, and Velocity of the β-particles (Electrons).—The particles of the β-rays, which are usually called electrons, are negatively charged. After eliminating the relativity influence, the ratio $\frac{e}{m}$ *amounts to* 1.769 10^7 *e.m u.*, or $5.31 \cdot 10^{17}$ *e s.u.* Under the assumption that the electron carries one elementary charge, it is found that *the mass of the electron is* 1850 *times smaller than that of a H atom,* since $\frac{e}{m}$ is 1850 times larger than for a singly charged H atom. Since such a small mass has not been found in neutral condition, it appears as if the mass of the electron was simply associated with its charge and thus forms an indivisible unit. It is even very probable that an electron is not to be considered as a mass in the usual sense, but as an **electromagnetic mass,** *i e , the inertia effects which the electron shows are dependent only on its electric charge.*

That an electrically charged body, apart from its ordinary mass, shows certain inertia effects, follows from the fact that its acceleration is associated with the production of a magnetic field; therefore, an electric charge without mass and at rest cannot be set in motion directly but requires an addition of energy which corresponds to the strength of the magnetic field produced This is the same phenomenon which is known as "self-induction" in the study of electricity.

If this idea is pursued further and the electron is considered provisionally as a small, rigid, metallically conducting, charged sphere, then certain statements can be made regarding its size

After a long calculation the following expression for the electromagnetic mass of a body is obtained:

$$m' = \frac{4\,U_e}{3\,V_l^2}$$

in which U_e is the electrostatic energy of the body For an electricall charged sphere of radius *a* with its charge evenly distributed over its surface we get:

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[1] *Phil. Mag*, **22,** 613 (1911); **23,** 439 (1912).

$$U_e = \frac{1}{2}\frac{e^2}{a},$$

from which follows

$$a = \frac{2}{3}\frac{e}{V_l^2}\frac{e}{m'}.$$

Now putting $e = e_0 = 4.77 \cdot 10^{-10}$, $\frac{e}{m'} = 5.31 \cdot 10^{17}$, we obtain

$$a = \frac{2 \times 4.77}{3 \times 9 \times 10^{20}} \times 5.31 \times 10^{7} = 1.88 \cdot 10^{-13}.$$

The radius of the electron is thus about 100,000 times smaller than that of the atom (*cf.* Table 66). No great stress is to be laid upon this value since the basis of the calculation which leads to it is not at all certain. If, however, it is possible to speak of a definite radius for the electron, it is most probable that it is even very much smaller than $1.88 \cdot 10^{-13}$ *cm*.

The velocity with which the electrons are expelled from the radioactive substance is relatively high; in some cases it approaches to within a few per cent of the velocity of light. The smallest velocity yet observed in a radioactive process (decomposition of RaD) is about one-third that of light. The electrons sent out by a definite radioactive transformation possess different velocities; yet these lie within narrow limits, so that the total β-radiation from a radioactive transformation may be fairly accurately characterized by means of single constant, *e.g.*, its absorption power in Al.[1]

282. The Magnitude of the Energy Change Involved in the Radioactive Processes.—As a result of their high velocities of emission, *a considerable amount of kinetic energy is inherent in the radioactive corpuscular rays.* Because of their greater mass, even though their initial velocity is lower, the energy of the α-particles is appreciably greater than that of the β-particles. The energy of a single α-particle with a velocity of $1.5 \cdot 10^{9}$ *cm./sec.* amounts to $\frac{1}{2} \times \frac{4}{6.06 \times 10^{23}} \times 2.25 \times 10^{18} \simeq 0.75 \cdot 10^{-5}$ *erg*. The enormous amount of this energy is better appreciated if given in terms of a gram-atom (4 *g*.); we then obtain $4.5 \cdot 10^{18}$ *erg* = $4.5 \cdot 10^{11}$ *watt-sec.* = $1.25 \cdot 10^{5}$ *kw.-hr.* = 14 *kw.-years.*

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[1] L. Meitner (*Z. Physik*, **9**, 131 (1922)) has recently shown that the complex character of the β-rays is probably due to the fact that the primary, homogeneous β-rays emitted during the radioactive disintegration give rise to the formation of secondary β-rays which have their source in peripheral electrons and not in the nucleus.

If the rays sent out by a radioactive substance are retained by a covering which they cannot penetrate, their kinetic energy is usually converted into heat, or, in other words, a certain amount of heat is continually developed in the material surrounding the radioactive substance. For 1 *g* of pure radium this amounts to about 25.2 *cal* per hour,[1] and, for radium in equilibrium with its four α-ray transformation products, to about 135 to 137 *cal.*

The energy liberated by a radioactive decomposition must previously have been stored up in some form. A radioactive atom, and apparently also the other atoms, must therefore possess an exceedingly large amount of internal energy. However, since the structures of the majority of atoms are relatively stable, their energy is unaffected by most physical and chemical changes, and therefore its presence is not made apparent.

283. Conclusions.—From the viewpoint of atomic structure, the corpuscular rays sent out in radioactive transformation indicate:

1. That atoms are to be considered as at least partially built up of electrons and doubly charged He atoms.

2. Since, according to the conclusions in **274,** the radioactive process takes place in the nucleus, the origin of the radioactive cleavage products is in the nucleus and not in the peripheral part of the atom.

c. Non-radioactive Emission of Electrons

284. The Constituents of the Outer Portions of the Atom.—The phenomena of radioactivity have given us a survey over the cleavage products of the atomic nucleus. The question of what constitutes the outer layers of the atom again presents itself. While the cohesion between the constituents of the nucleus is so strong that the ordinary chemical and physical procedures do not tear them apart, it might be expected that the constituents of the outer layers of the atom would be easier to separate, and, conversely, that the origin of those elementary particles, which are relatively easily removed from the atom, is to be sought in the periphery. It may be assumed at the start that it is only necessary to demonstrate that the particles which can be easily separated from the atom by various physical and chemical influences are electrons. This gives us directly a provisional conception of the atom *as a nucleus surrounded by a number of electrons, a sort of "electron cloud" Since the electrons are negatively charged and the whole atom is electrically neutral, the nucleus must carry a positive charge corresponding to the number of electrons* in the periphery. Further, since the electrons possess only a very small mass, the greater part of the mass must be concentrated in the nucleus, a conclusion which has already been reached (see **274**) from another viewpoint

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[1] Quantitatively considered, this heat energy corresponds very closely to the kinetic energy of the α-rays emitted by 1 *g* of Ra when the velocity of the rays is $1.51 \cdot 10^{9}$ *cm/sec.* The radioactive constant for Ra is $\frac{0.693}{1580 \times 8750} = 0.502 \cdot 10^{-7}$ *reciprocal hours* (*i.e.*, in 1 *hr* the fraction $0.502 \cdot 10^{-7}$ of the Ra disintegrates). One gram of Ra contains $2.68 \cdot 10^{21}$ atoms; therefore $1.34 \cdot 10^{14}$ atoms disintegrate in 1 *hr*. The corresponding energy is $1.02 \cdot 10^{9}$ *erg* or 24.4 *cal* which is a good agreement with the directly determined value.

285. Thermal Emission of Electrons from Heated Bodies.[1]—In many cases it is only necessary to heat the substance to a sufficiently high temperature to set electrons free from the atoms This phenomenon is called the **thermal emission of electrons.** Metals like tungsten, and especially metallic oxides, when heated to high temperature usually send out considerable quantities of electrons which, in comparison with the β-particles from a radioactive β-transformation, have very low initial velocities.

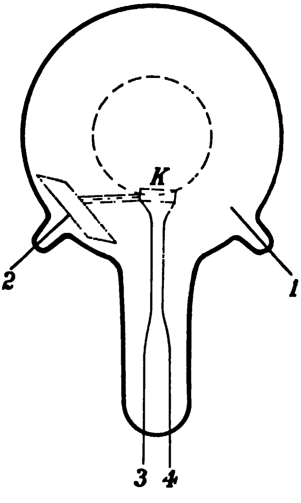

Fig. 61

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[1] * For a detailed discussion of this subject see Richardson, O. W, "The Emission of Electricity from Hot Bodies," Longmans, Green & Co (1916); and Foote and Mohler, "The Origin of Spectra," chap VII, Chemical Catalog Co. (1922).

The proof that the same kind of particles (electrons) are really sent out by a glowing body as by a radioactive β-transformation follows from the use of a Wehnelt tube (Fig. 61) which is not too highly evacuated (pressure approximately 0.1 *mm.* Hg).

The oxide, coated on a Pt foil, is placed at the point K and is heated to a glowing temperature by a low-tension current through the foil entering at 3 and 4. The electrons emerging at K are then accelerated by an electric field between K and the electrode 1 or 2, so that their velocities are greatly increased. Equation (258*a*) gives the relation between this velocity V and the value of $\frac{e}{m}$, the latter being still regarded as unknown.

The beam of electrons appears in the tube as a narrow sky-blue band, the color being due to the flashes resulting from the collision between the electrons and the gas molecules. If a magnetic field is now allowed to act upon the tube, so that the magnetic lines of force are perpendicular to the plane of the paper (see Fig. 61), then the electron beam will bend, as indicated in the figure, into a circle of greater or smaller diameter, depending on the strength of the magnetic field. The direction of the deflection indicates that the particles of the ray must be negatively charged By using Eq. (260) along with Eq. (258*a*) $\frac{e}{m}$ and V can be calculated For the specific charge the result is $\frac{e}{m} = \frac{2E}{H^2r^2}$ Later measurements, applying all precautions and considering all correction factors, give the value of $\frac{e}{m}$ as $1.765 \cdot 10^7$ *e.m.u.*, which is in excellent agreement with the value given above for the β-ray particles.

In order to measure the number of electrons given out by a glowing body in unit time, the following arrangement may be used: the glowing body—preferably a wire of a difficultly fusible metal heated by a low-tension current—is surrounded by a metal plate or netting (the Faraday cage), both contained in a highly evacuated vessel. On account of the influence of the traces of gas originally occluded by the metal wire and driven out by the heating, it is best to evacuate the tube highly during the entire experiment. The metal plate now becomes negatively charged compared to the wire, as can be shown by an electrometer. If the metal plate is given a charge of a few volts positive to the glowing wire, then *all* the electrons sent off by the latter will be rapidly assisted over to the plate and be discharged. Thus a negative current flows between the wire and the plate; its intensity depends only on the number of electrons liberated in unit time, and is therefore independent of the difference of potential. We have here a phenomenon which is in complete analogy with the "limiting current" discussed in **251.** In the present case, this current, which is independent of the potential difference, is called the **saturation current.** If the plate is charged negatively, no current flows, since electrons cannot move towards a negative potential. This is a very simple and distinctive case of *unipolar conduction.*

If the temperature of the glowing wire is changed, the strength of saturation current I_0 or the number of electrons N' liberated *per second* usually changes considerably, according to a formula advanced by Richardson in 1901 but which became fully appreciated only in recent times as the result of careful measurements by Langmuir (1914). This formula is:

$$I_0 = N'e_0 = a\sqrt{T} \cdot e^{-\frac{b}{T}}$$

or

$$log\ N' = -\frac{b}{T} + \frac{1}{2}\ log\ T + Const., \qquad (264)$$

in which a and b are constants; a depends upon the particular apparatus used, but b is independent of this factor.

The analogy of Eq (264) to the ordinary vapor pressure Eq (131*f*) has led to considering the emission of electrons directly as a sort of vaporization process, and therefore the term **electron vapor pressure** of heated bodies arose It has been attempted to treat the free electrons thus entering into a vacuum (at first unaccelerated) theoretically as an ideal gas

Taken as a whole, this conception has been shown to be appropriate, even if in individual cases the theory meets with difficulties in its application.[1] Of course, it is certainly not permissible to apply the gas laws to the "electron vapor" for the purpose of exact calculation, since an ideal gas is distinguished by the absence of forces between its molecules, whereas between the free electrons very considerable repulsive forces are at work.

[1] M v. LAUE, *Jahr Radioakt Elektronik*, **15,** 208, 255 (1918) * SAHA, *Phil Mag*, **40,** 72 (1920). * TOLMAN, *J. Am Chem. Soc.*, **43,** 1592 (1921).

If, in spite of this, the ideas which were developed for the consideration of the vaporization process in liquids are applied directly to the present case, one is forced to the assumption that the force (which, moreover, must not be too powerful) with which the peripheral electrons are bound to an individual atom in the gaseous state is considerably diminished in the solid state by the influence of the neighboring atoms. Van der Waals' theory involved a similar assumption that no force is exerted upon an atom in the interior of a liquid (*i e*, not at an interface) due to the compensating effect of the neighboring molecules, at least, when in a definite position of equilibrium In this way the conception develops, which is of especially great importance for the theory of metallic conduction, that the electrons within metals or solid bodies, *e g*, oxides (*cf* GERMERSHAUSEN, *Ann Physik*, **51**, 705 (1916)), move almost without restriction and thus in many respects behave similarly to the molecules of a gas When an electron leaves a metal, a certain attractive force in the surface layer must be overcome, just as in the evaporation of the molecules from a liquid, *i e*, a certain amount of work must be performed against the force of attraction This work may be readily calculated if the concentration c_i and c_a of the electrons inside and outside the metal are known In case the gas law is applied directly to the inner and outer electrons, Eq (78) for the work of expansion of a gas,

$$A = RTln\frac{c_i}{c_a} \quad \text{or} \quad c_a = c_i e^{-\frac{A}{RT}}, \qquad (264a)$$

must hold, since the inner electrons must certainly be in greater concentration than the outer electrons on account of the force of attraction Now consider, as a hypothetical case, a cylindrical section within a solid block of metal Assume that in some way the cylinder is fitted with a movable piston and contains only a number of inner electrons free from metal atoms Now gradually move this cylinder, together with its piston, away from the metal, the electrons in the act of leaving the metal surface must expand, and the movement of the piston due to this expansion can be applied to performing the amount of work required by Eq. (264*a*) But since, in reality, the electrons leave the metal individually, it is impossible to obtain the molecular energy directly as mechanical work, just as it is impossible in the evaporation process; the molecular energy indicates its presence only as a heat effect Thus A in Eq (264*a*) must be regarded as the *heat of evaporation of electrons*

In the state of equilibrium, for which Eq. (264*a*) holds, the number N' of electrons leaving the metal *per second* (which depends on the saturation current) is equal to the number of electrons which enter the metal from outside and are again absorbed by it. The number is greater, (1) the greater the outer concentration c_a, and (2) the greater the velocity. If the latter quantity is considered to be proportional to the square root of the absolute temperature, similar to a gas (*cf.* **50**), and by applying Eq. (264*a*), we then get

$$N' = Const. \cdot c_a\sqrt{T} = Const. \cdot c_i\sqrt{T} \cdot e^{-\frac{A}{RT}}, \qquad (264b)$$

which corresponds exactly to Eq. (264) if it is assumed that the concentration of the inner, "free" electrons is independent of the temperature. The heat of vaporization of the electrons may be calculated from the experimental value of b; ($A = bR$), and for various substances values between 50 and 150 *cal.* are obtained. Further, Eq. (264*b*) may be derived directly from Eq. (135), since the quantity B appearing in the latter is proportional to the square root of T

286. Dissociation of Heated Gases into Electrons and Ions.—The spontaneous separation of electrons from heated bodies can be considered as a thermal dissociation of the atoms. In order to establish the parallelism between this process and that of the ordinary chemical dissociation of dissolved or gaseous molecules, it was necessary to prove that gaseous atoms dissociate directly into positive ions and electrons at high temperatures. This latter phenomenon actually does occur, as was first shown by Lenard (1902); the appreciable conductivity of flames is, to a large extent, due to the presence of free electrons.[1] Even if a part of the electrons should result from the chemical reactions taking place in the flame, the greater part is without doubt of purely thermal origin. For this viewpoint it is especially significant that the conductivity of a flame is considerably increased by the addition of the vapors of metallic salts which do not take part in the combustion but whose atoms possess a strong tendency to dissociate off electrons.

287. Ionization by Impact of Corpuscular Rays.—While at high temperatures electrons dissociate spontaneously from atoms, a certain addition of energy is required to set them free at ordinary temperatures.

It is clear that the energy of an α-ray or a β-ray particle, as well as that of an electron which has been artificially accelerated in a strong electric field, must easily be sufficient to break loose electrons by collision with neutral atoms. That such is really the case is evident from the strong ionization produced by all corpuscular rays passing through air or other gases. The primary process in the collision of an α- or a β-particle with an atom is undoubtedly the separation of one or more electrons. That the process can in no way be considered as involving only the electrons at the surface of the atom, but also some in the deeper layers, if not with the nucleus itself, is not astonishing, considering the large energy content of the individual particles of the corpuscular rays (see **325**).

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[1] A summary of these phenomena is given by A. Becker, *Jahr. Radioakt Elektronik*, **13**, 197 (1916); * Wilson, H. A., "Electrical Properties of Flames and Incandescent Solids," London University Press (1912); Thomson, J. J., "Conduction of Electricity through Gases," chap. IX, Cambridge University Press (1903).

It frequently happens that the electrons torn loose from an atom by collision have such a high velocity that they are able to liberate electrons from other atoms. If the gas which has been exposed to the action of corpuscular rays is put in a strong electric field, then all the electrons, even those which were originally slow-moving, are much accelerated, so that subsequently they also acquire the ability to liberate electrons from other atoms. By means of this phenomenon, called **ionization by collision or impact,** it is possible to magnify to an extraordinary degree the original number of ions produced by the single α- or β-ray, so that a single α-particle or even a single β-particle suffices to give a measurable deflection on a sensitive galvanometer.

The passage of the electric current through moderately evacuated discharge tubes (the Geissler tubes) likewise depends mostly upon ionization by impact The electrons, which are only sporadically sent out by the cathode at ordinary temperatures, are accelerated by the potential difference in the tube (in the dark space existing around the cathode this is especially high), so that after a time they are able to liberate electrons from the gas molecules. These are, in turn, accelerated and act upon other molecules. Finally, so many electrons exist that the gas becomes perceptibly luminiscent, due to the collisions between the electrons and the gas molecules. At a somewhat higher vacuum the electrons produced in the vicinity of the cathode strike the opposite glass wall and cause a fluorescence, a phenomenon discovered by Pluckner (1858). The properties of the electronic rays produced in this way were first investigated by Hittorf (1869) and Goldstein (1876); the latter named these rays **cathode rays** because of their origin. By means of these rays science first became better acquainted with **free electrons.**

This "knocking off" of electrons by powerful corpuscular rays can be shown not only in gaseous substances but also in solids. Every point where α-rays strike the walls of the vessel, etc. is the origin of new radiation, called the δ-rays, which consist of relatively slow-moving, easily deflected electrons.

288. Liberation of Electrons by Illumination.[1]—Finally, electrons may be liberated from atoms by illuminating them with light (using the term in its broadest sense). The important laws connected with this form of electron emission, the so-called **photoelectric effect,** will be considered in detail in one of the following sections. Here it needs only to be noted that strongly electropositive metals, which have a special tendency towards forming positive ions, *e g* , the alkali and alkaline earth metals, send out electrons even under the illumination of visible light, while other metals first show the photoelectric effect in the ultraviolet light. An especially strong emission of electrons results from the X-rays, which have wave lengths about 1000 times smaller than ordinary light (*cf* **299**). The electrons liberated by the X-rays, and which thus acquire a considerable velocity, are usually called the **secondary cathode rays,** since they were quite soon recognized to be identical with the ordinary cathode rays.

The photographs of the secondary rays, taken by C. T. R. Wilson according to the method described above (see **277**) after illuminating air with X-rays, are instructive (Fig. 62, page 501). A glance at this figure shows that no appreciable ionization takes place directly by means of the X-rays, otherwise the cloud particles, which correspond to the gas ions, and which appear as small white points in the picture, must be equally distributed. Ionization can be observed exclusively along the zigzag paths of the secondary cathode rays.

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[1] * See also the monographs by HUGHES, "Photoelectricity," Cambridge University Press (1914), and ALLEN, "Photoelectricity," Longmans, Green & Co (1913); a more modern theoretical treatment is given by FOOTE and MOHLER, *loc. cit.*

f. THE SIZE AND CHARGE OF THE NUCLEUS

289. The Passage of Corpuscular Rays through Matter.—Important conclusions concerning the size and the charge of the atomic nucleus may be drawn from the manner in which corpuscular rays, particularly the rapidly moving rays, are absorbed or scattered by matter.

If slow corpuscular rays, produced within a potential difference of at most 6 *volts*, are allowed to strike gas molecules, the particles will simply be reflected or scattered by the gas molecules, provided they do not unite to form ions. From this the effective molecular diameters are found to be approximately the same as the values given by the various methods based on kinetic theory (see **261**); the result is the same whether the corpuscular rays consist of electrons or positive ions.[1]

Rapid corpuscular rays, such as cathode, α-, and β-rays, behave quite differently. Such rays are able, as has already been mentioned, to penetrate relatively thick layers of material such as metal foil. A beam, sharply defined originally, becomes somewhat diffuse and the velocity of the particles is decreased, but the number of particles is practically unchanged as long as the velocity is fairly high

Since the results of the older kinetic theory of matter consistently lead to the idea that atoms or molecules in the solid state leave only a small amount of "free space" between them (*cf.* **261**), it must be concluded that *the particles of the corpuscular rays penetrate the atoms*, whereby they, of course, suffer a loss of energy, but are, in general, also slightly deflected from their original direction. An α-particle must strike a very large number of atoms before its energy is completely absorbed. The mean free path of an α-particle (assumed to be a point) in air at atmospheric pressure is about $4 \cdot 10^{-5}$ *cm*[2] The particle meets about 25,000 air molecules in a path 1 *cm* long, or a total of 100,000 molecules during its range or existence of 4 *cm*. While with respect to other slow-moving molecules and electrons atoms and molecules behave as an inpenetrable system because of their mutual collisions, the preceding statement indicates that such a system offers only a relatively small resistance to particles moving with great velocity.

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[1] However, with still slower electronic rays, Ramsauer (*Jahr Radioakt Elektronik*, **19**, 345 (1923)) found with decreasing electron velocity first an increase, then a sharp decrease in the effective (apparent) molecular diameter A satisfactory theoretical explanation of this striking result has not yet been found.

[2] The value quoted in **53** refers to the mean free path of an N_2 or O_2 molecule in air; that of a point in air must be four times as great, according to the kinetic theory of gases.

Other things being equal, the *slight diminution in the velocity of a particle passing through a single atom becomes greater as the weight of the absorbing atom increases.* This is especially true in the case of cathode rays. Lenard (1903) concluded from this that the absorption or scattering was caused by fields of force (with very small effective range) inside the atom, which he called "dynamides" and the total number of which he assumed to be proportional to the atomic weight. It is to be noted that this "dynamide" theory of Lenard is completely in line with the present theory of atomic structure if the "dynamides" are considered the same as electrons of the outer electronic regions (*cf.* **291**).

290. The Deflection of an α-particle during the Penetration of an Atom.—For the accurate, quantitative measurement of the phenomena of the penetration of matter by corpuscular rays, the α-rays are much more suitable than the electron rays.

In general, the α-rays show a very slight change of direction, amounting to only a few degrees, during their passage through matter. But, on the other hand, very great changes of direction sometimes occur under certain conditions and individual particles may even be deflected backwards. These sporadically occurring, large changes of direction are particularly important They are perceptible in Wilson's photographs (Figs 58 and 59), being indicated by sharp breaks, since every such change of direction is the result of a single collision. While it must be assumed that the slight changes of direction which most of the α-particles show is due to an influence of the electronic region of the penetrated atom, Rutherford (1911) developed the idea that *the large deflections which occur occasionally are the result of a collision between an α-particle and an atomic nucleus.* This conception leads to the qualitative result:

1. That the atomic nucleus must be very small, since "collision" occurs so seldom.

2. That extraordinarily large forces come into play at each collision.

To obtain a formula by which his fundamental assumptions could be tested experimentally, Rutherford further assumed that the nucleus was a point and that merely the electrostatic repulsive forces of Coulomb's law act between the nucleus and the particle. The calculation of the path which an α-particle describes about the nucleus (one cannot consider it as a real collision) takes exactly the same form as that for the path of a comet around the sun. The equations remain unchanged in form, since the Newtonian law of attraction represents the same function of distance as Coulomb's law. Although as a first approximation both the comet and the α-particle describe hyperbolas, the difference between the two cases lies in the fact that the comet travels *around* the sun due to the force of attraction (from the standpoint of the sun it describes an angle greater than 180 deg.), while the α-particle, due to its repulsive force, remains on the one side of the nucleus (describes an angle less than 180 deg.). The behavior of an α-particle on its approach to a nucleus is made clear by Fig 63. The closer the α-particle approaches the nucleus the greater is the deflection. As a result of the assumed

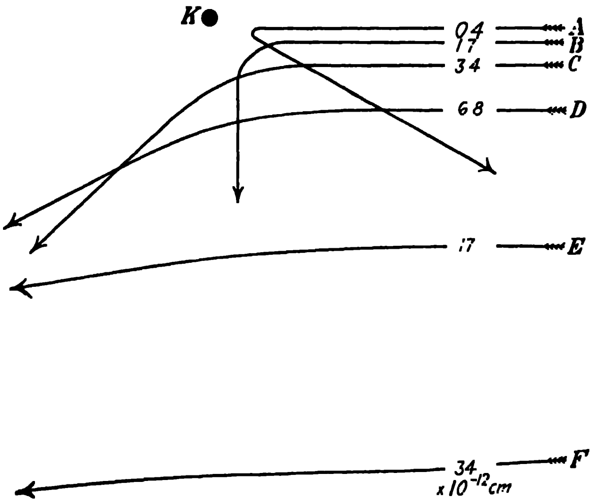

Fig 63

point-like forms of the deflecting nucleus and of the α-particle, and the extraordinarily great velocity of the latter, the deflection reaches a perceptible amount only if the α-particle approaches very close to the nucleus.[1] Figure 63 gives an approximate picture of the actual relation if it is imagined that the total diameter of the atom, when drawn on the same scale as the figure, will be about 100 *m*. The figure thus illustrates only the immediate neighborhood of the nucleus

If a large number of deflecting atoms (N per unit volume) is considered, the following formula is finally obtained:

$$y = \frac{N\delta \cdot e_k^2 \cdot e^2 Q}{L^2 \cdot 16 \cdot r^2 \cdot sin^4 \frac{\varphi}{2}}, \tag{265}$$

in which y is the number of α-particles striking a unit area of a collecting surface per second, the particles in passing through a dispersing layer of thickness δ being deflected through the angle φ. The constants appearing in this formula have the following significance: Q is the total number of α-particles striking upon the dispersing layer; e_k the charge on the nucleus; e the charge on the α-particle; L the kinetic energy of the α-particle; and r the distance from the dispersing layer to the collecting or indicating surface.

TABLE 72.—SCATTERING OF α-RAYS BY A GOLD LEAF $^1/_{1000}$ *mm* THICK

Angle of deflection, degrees	Number of impinging α-particles	$\frac{1}{sin^4 \frac{\varphi}{2}}$	$y\, sin^4 \frac{\varphi}{2}$
5	276300	8320000	31
10	17330	503000	29
15	3445	121000	35
30	223	7800	35
45	46.6	1435	31
75	7.25	211	29
120	1.79	52	29
150	1.15	33	29

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[1] The number beside each arrow in Fig. 63 indicates the shortest distance between the nucleus and the particle, provided the latter passed by the nucleus without being deflected.

As the above table shows, the dependence of the number y on the angle of deflection φ $\left(y \cdot sin^4 \frac{\varphi}{2} = Const\right)$ was strikingly confirmed for heavy atoms by the careful investigations of Geiger and Marsden, so that the correctness of Rutherford's assumptions may be considered as proved and the application of Eq. (265) to other problems thus seems to be justified.

For heavy atoms with large nuclear charges the nearest an α-particle can approach the nucleus is about $3 \cdot 10^{-12}$ *cm.* from the midpoint of the nucleus In these cases no deviations from Eq (265) can be observed, *i e*, the nucleus and the α-particle behave towards each other like electrical point centers of mass for which Coulomb's law holds

Collisions with lighter atoms, where α-particles can approach much closer to the nucleus because of the smaller charge on the latter, show deviations from Eq (265). From this it must be concluded that the assumptions are not correct at distances of about $5 \cdot 10^{-13}$; the repulsion below this limit becomes stronger than Coulomb's law requires Therefore, $5 \cdot 10^{-13}$ may be considered as an approximate value for the nuclear diameter of the lighter atoms, if it is at all possible to speak of a definite diameter for the nucleus.

291. The Nuclear Charge, ***Z.***—Except the charge on the nucleus e_l, all the values occurring in Eq (265) can be determined experimentally or can be assumed to be known. This formula thus offers the possibility of determining the number of charges on the nucleus $Z = \frac{e_l}{e_0}$, that is, the ratio of the nuclear charge to the elementary electrical charge By measuring the dispersion or "scattering" by various substances it was found that the nuclear charge number is equal to about one-half the atomic weight:

$$Z \simeq \frac{A}{2}.$$

In this way it was first possible to obtain a quantitative expression concerning the charge on the nucleus and thus the number of electrons surrounding it.[1]

In 1913 van dem Broeck expressed the supposition, based upon observations upon the periodic system, which was later shown to be partially incorrect, that the nuclear charge number was not exactly one-half the atomic weight, but was to be set equal to the number denoting the position of the element in the periodic system, or, in other words, *the nuclear charge number and the atomic number had the same value.* Later, Chadwick (1920), by repeating the Geiger-Mardsen investigations with greater experimental accuracy, succeeded in confirming this statement quite satisfactorily; from the deflection experiments he found for Pt, $Z = 77.4$ instead of 78; for Ag, $Z = 46.3$ instead of 47; for Cu, $Z = 29.3$ instead of 29.

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[1] Due to unavoidable inaccuracies in the fundamental investigations, this first expression was, of course, only approximately constant

The fruitfulness of this idea was proved in a most exact, quantitative way by the regular displacement of the X-ray spectra with increasing atomic number (Mosely; see **323**). The previously discussed radioactive displacement law (see **271**) is also in excellent agreement with this idea. Sending off a β-particle robs the nucleus of a negative charge; *i e*, the nucleus becomes one unit more positive; but on the basis of the change of chemical properties of an atom due to a β-transformation, its atomic number must be increased by one unit. On the other hand, an α-transformation lowers the nuclear charge by two units, and the change of chemical properties corresponds to a diminution of the atomic number of two units.

Thus in one stroke the solution of the *total number of electrons* in the outer "electron cloud" is found; it *is simply equal to the nuclear charge number or the atomic number*, since the whole atom must be electrically neutral and there are no positive charges outside of the nucleus[1]

The periodic system thus begins at hydrogen with a nuclear charge of 1 and a single outer electron, and from this point increases from element to element by unit steps. *Isotopes are distinctive in that they possess the same nuclear charge and the same number of outer electrons, but differ from each other in the structure and the mass of the nucleus.*

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[1] From the results of Barkla's investigations of the intensity of X-rays scattered by different elements, J J Thomson, as early as 1906, calculated that for the lighter elements the number of outer electrons effective in scattering the rays was equal to half the atomic weight Although this calculation was based on classical laws, it is to be considered as essentially correct even today (see LADENBURG and REICHE, *Die Naturwissenschaften*, **11**, 597 (1923).

292. Swift Hydrogen Particles.[1]—In Rutherford's theory of the deflection of an α-particle by an atomic nucleus nothing has yet been said concerning the fact that the nucleus itself is also set in motion by the approach of the α-particle. With the heavier atoms, this will not appreciably influence the deflection of the α-particle. On the other hand, the lighter atoms, especially hydrogen atoms, will attain a very considerable velocity in such a collision, so that they will be hurled forward and, like the α-particle itself, are for a time able to ionize the air along their paths. The range of these **swift hydrogen particles** is even considerably greater than that of the α-particles; their range in air is 28 *cm.*, while the range of the α-particles producing them is about 7 *cm.*

This effect, which was first described by Marsden, has been photographed by D. Bose,[2] using Wilson's arrangement (see **277**). Figure 64, page 502, a reproduction of such a photograph, shows that a new ray starts from a definite point in the path of an α-particle, and the α-particle itself is deflected a little from its path. An effective collision leading to the formation of a hydrogen particle occurs extremely seldom. Rutherford has found that the mean distance through which an α-particle must travel in hydrogen before a swift H particle is set in motion is about 10^5 *cm.* Since this distance is considerably greater than the range of the α-rays, it signifies that not every α-particle gives rise to the formation of a rapid H particle. Now each α-particle strikes about 10^4 H atoms in traveling a distance[3] of 1 *cm.* and it follows, therefore, that only one out of 10^9 collisions is effective. The earlier conclusions with regard to the smallness of the nuclear dimensions are thus confirmed. The force at the moment of collision (even if for only a short time) is very great; according to Rutherford it amounts to about 5 *kg.* for two single particles.

293. Splitting Off Hydrogen Atoms from Other Elements.—In his experiments on the effect of the α-rays on other atoms, Rutherford found that when elementary N or a nitrogen compound was subjected to the action of these rays, H rays also appeared. The identity of these rays was established with certainty first by their enormously long range (28 *cm.*) and later by the determination of the ratio $\frac{e}{m}$. The possibility that the source of the H rays might be traces (impurities) of hydrogen compounds was eliminated with the greatest care; therefore, the H rays must have had their origin in the nitrogen atoms, and it was now for the first time possible to decompose an atomic nucleus artificially. An effective collision between an α-particle and a nitrogen atom, producing an H particle, also occurs extraordinarily seldom, a single H particle being set free only in about 10^{15} collisions.

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[1] * Sometimes these are called the *long-range hydrogen particles.*

[2] * *Physik Zeit*, **17**, 388 (1916).

[3] This number is smaller than for air, since the radius of the H atom, based on the kinetic theory of gases, is smaller than that of N and O.

In more recent work Rutherford and Chadwick[1] succeeded in proving that H atoms were liberated by the collision of α-particles with a number of other atoms, namely, boron, fluorine, sodium, aluminium, and phosphorus. Strange to say, the range of these H rays is sometimes considerably greater than is produced in pure hydrogen; for Al, the range is between 67 and 90 *cm*; for B, 38 to 58 *cm.*; for N, 18 to 40 *cm.* according as the H rays are in the same or opposite direction to the α-rays producing them. Since the energy of the impinging α-ray is not sufficient to impart such a velocity to the H atom, one is led to the idea that the striking of an α-particle is necessary for the destruction of an atomic nucleus, but that an important part of the energy propelling the H atom comes from the nucleus itself. In the forced decomposition of heavy nuclei into He and H nuclei it thus appears that energy is liberated just as in the spontaneous, radioactive disintegration; the combination of He and H nuclei therefore represents an endothermic process.

From the splitting of H nuclei from nitrogen and several other elements, a real experimental basis for Prout's hypothesis is again obtained. It is worth noting that up to the present time H atoms have been split out of other atoms only when the atomic weights of these atoms were approximately equal to $4n - 2$ or $4n - 3 (n = 1, 2, 3, \ldots)$, while those elements with atomic weights of approximately $4n$ have as yet yielded no H atoms.[2]

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[1] *Nature*, **107**, 41 (1921); *Phil Mag.* (6), **44**, 417 (1922).

[2] * This directly involves the question of nuclear stability The radioactive disintegration of the heavier atoms as well as Rutherford's experi-

In an element of atomic weight $4n - 3$, it would therefore appear as if only the number 3 corresponds to the H atoms, while the number $4n$ indicates the presence of n helium nuclei. In this there is a new confirmation for the conclusion that the helium atom plays an independent rôle in the structure of atoms, which had already been definitely established by the radioactive phenomena.[1]

Rutherford's results provide a basis for the theory of the structure of the atomic nucleus.[2] Detailed calculations have already been made, especially upon the helium nucleus, which can be considered as being formed from four H nuclei and two electrons, and to which an especially high stability must be ascribed since it appears to remain undamaged after all its collisions with other nuclei. The great stability of the He atom further shows that the combination of H nuclei to form a He nucleus must be strongly exothermic (*cf* **276**).

If, however, the union of H and He nuclei to form the nuclei of heavier atoms really represents an endothermic process, as must be assumed from Rutherford's results, the atomic weights of the atomic species in question, especially Al, must be appreciably greater than whole numbers. At the present time we actually have, as the most probable atomic weight of Al, the value 27 1 (Al has no isotopes) but lower values have been found recently (see Landolt-Bornstein, fifth edition)

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ments on the lighter atoms indicates that all nuclei are not equally stable Harkins (*Phil Mag*, **42,** 305 (1921)), in a statistical investigation of the distribution of atomic species in the earth's crust and meteorites, finds that atoms with even values of Z are more abundant than those for which Z is odd, and further that about thirteen atoms out of fourteen have atomic masses divisible by 4 See also Andrade (*loc cit*, p 112), where an interesting table indicating the instability of certain atomic masses will be found. In a long series of articles (*J Franklin Inst*, **194,** 165, 329, 521, 645, 783 (1922)), Harkins discusses the stability of atomic nuclei in great detail

[1] * Aston ("Isotopes," p 102 *et seq*) gives several reasons why the helium atom as such should *not* exist in the atomic nucleus

[2] * There is evidence from the γ-rays for the existence of definite energy levels within the nucleus similar to those of the electronic orbits (see **296** *et seq*) See C. D Ellis (*Proc Roy Soc* (A), **101,** 1 (1922)), who discusses this evidence and gives numerous references to the work of Rutherford and his co-workers

3. ENERGY EXCHANGE IN ATOMIC AND MOLECULAR PROCESSES

a. The Liberation and Absorption of Energy in the Form of Energy Quanta

294. General.—In the preceding section it could be demonstrated that the atom consisted of a nearly point-like nucleus which contained the total mass and carried a charge of Z units, the nucleus being surrounded by Z electrons The arrangement of these electrons must now be examined more closely.

Since the nucleus is strongly charged positively, the first question concerns the method by which it is possible for the negatively charged electrons to remain independent of the nucleus and not unite with it in spite of the electrostatic forces of attraction The explanation is the same as for the reason why the planets do not fall into the sun, even in spite of the gravitational forces. It is assumed that the *electrons move in circles or ellipses around the nucleus, and that the centrifugal force at every moment compensates for the attraction.*

In this way the fundamental conception is obtained that *the atoms are planet systems of very small orbits, in which the sun is replaced by the nucleus and the planets by the electrons*

295. Electronic Motion Which Does Not Involve Radiation.—Even though this conception is very attractive, certain objections arise which are important in that they must be removed in some way, even violently, by the introduction of new hypotheses if the planetary system is to be retained as the atomic model.

The most difficult of these objections is *that a rotating electron, similar to every other accelerated electrical charge, should continuously send out radiation with which a loss of energy must be involved.*

That an electron rotating about the nucleus actually must radiate may be qualitatively illustrated by the following example. The vibration of a tuning fork gradually decreases mainly because the vibrations have been transferred to the surrounding air and conducted away as sound waves; if an isolated electric point charge should be fastened to the end of a vibrating tuning fork, an electric "oscillator" would be obtained which exercises an effect upon the surroundings similar to an alternating current flowing in the path of vibration. As is well known, this first induces an alternating electric field in its immediate surroundings and the latter, in turn, induces a new magnetic field, etc. Thus an electromagnetic wave is generated, which, of course, requires a certain expenditure of energy for its production.[1] This energy can only be taken from the kinetic energy of the moving charge located on the tuning fork, *i.e.*, the motion of this charge will be "braked down" or "damped" by the sending out (radiation) of these electromagnetic waves. According to this idea, which is based upon the fundamental laws of the classical electrodynamics, which, in turn, were completely established by investigations upon larger (macroscopic) electrical oscillators, the electrons moving in their circular and elliptical orbits about the nucleus must likewise radiate energy. Therefore, their motion would gradually become slower due to the loss of energy; their orbits would become smaller and smaller until finally union with the nucleus would become unavoidable.[2]

But if it is required that the electrons in the normal paths are not to undergo a "damping" by radiation, it will mean nothing other than that *the ordinary classical laws of electrodynamics are no longer valid for the inner portions of the atom* [3]

Therefore, there are only two possibilities: either the idea of an atom modeled on the planetary system and based upon electrostatic attraction and centrifugal force must be dropped, or a limitation to the radiation laws when applied to electronic motion must at least be assumed. Since the former of these possibilities would remove every basis for further investigations of the atoms—for this special purpose, it would be necessary to introduce, in place of the centrifugal force, such repulsive forces as would prevent the electrons from falling into the nucleus—the largest part of modern investigation has decided, even though with hesitation, to adopt the second.[1] Later, in the discussion of the detailed structure of the planetary model, it will be shown that this step has been entirely justified.

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[1] With respect to the energy requirements of electric waves, it may be recalled that the production of the powerful waves such as are used in wireless telegraphy may require hundreds of horsepower.

[2] As is known, this fate would be assigned to the planets as compared to the sun, if their motion was checked by some means such as friction.

[3] This requirement can be avoided if it is assumed that the electron associated with an atom does not remain point-like but broadens out into a ring, for an electrically charged ring rotating on its own axis does not radiate energy. Since the point-like form of the electron is known only outside of atoms (in relatively weak fields of force), this possibility still deserves to be kept in mind.

The nucleus must also be considered as being similar to the outer regions of the atoms (the electronic "atmosphere"). The radioactive processes indicate that the nucleus must contain enormous amounts of energy within itself. If the assumption of unknown forces is to be avoided and if only electrical and centrifugal forces are to be considered, then it must be recognized, just as in the above, that an energy radiation is impossible, even if there are electrical charges in the liveliest motion in the interior of the nucleus.

296. The Discontinuity of Energy Changes in the Interior of the Atom.—*A fundamental distinction between a planet system and an atom exists in that, theoretically, a planet can travel on any course whatever around the sun, while for an electron revolving around a nucleus only a limited number of paths are stable.* The necessity of this law results directly from the following:

The various orbits of an electron differ from each other mainly in their energies.

The energy of a revolving planet (electron) consists of both kinetic and potential energy and, according to a given law of force, a constant ratio will exist between the two forms. According to Newton's or Coulomb's law of force, ($+\frac{e_k e_0}{a^2}$; (e_k, charge on the nucleus; a, distance from electron to nucleus), the potential energy, as is known, amounts to $-\frac{e_k e_0}{a}$; for the kinetic energy we have $\frac{1}{2}mV^2$ as usual. Since the centrifugal force must equal the force of attraction, we have $\frac{e_k e_0}{a^2} = \frac{mV^2}{a}$ and, therefore, $\frac{1}{2}mV^2 = \frac{e_k e_0}{2a}$, so that for the kinetic energy we get the value, $\frac{1}{2}\frac{e_k e_0}{a}$. The total energy thus amounts to

$$U = U_p + U_k = -\frac{e_k e_0}{a} + \frac{e_k e_0}{2a} = -\frac{1}{2}\frac{e_k e_0}{a} = -\frac{1}{2}\frac{A'}{a}. \quad (266)$$

---

[1] An atomic theory developed especially by G N Lewis and I Langmuir actually does depend upon the assumption of such forces, but it does not accomplish at all the same sort of things, especially what is demanded by the explanation of the optical properties of atoms, as the theory discussed in this book and which is due mainly to N. Bohr.

For $a = \infty$, U becomes 0; on the approach of the electron to the nucleus (a becomes a finite value) the system performs work, and the energy supply of the system decreases, which explains the negative sign of U.

Now, if all the orbits in an atomic planetary system were stable, then within certain limits it must be possible to add any optional amount of energy to the aton. However, a large number of experimental facts indicate that *the interior of the atom*, just as for the atom as a whole (at least, if it performs a vibrating or circular motion), *is able to absorb energy only in certain, definite quantum-like amounts*

This quantum-like energy absorption is shown perhaps most directly by the investigations of J Franck and G. Hertz (1912),

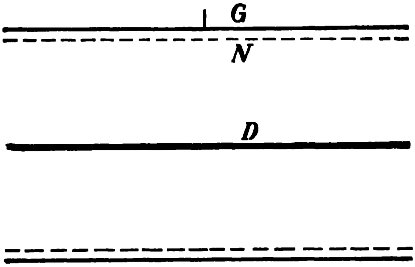

Fig. 65

in which the energy exchanges occurring at the collision of electrons with atoms were observed.

If a velocity (kinetic energy) is imparted to an electron and is gradually increased, it can be shown that up to a definite limiting velocity it will be reflected with complete elasticity (*i e*, no loss of energy) from a very large number of atoms. Above this limit a sudden inelastic collision occurs such that the total energy of the electron is absorbed by the atom and the electron is left with a zero velocity.

The experimental arrangement used by Franck and Hertz depended upon the following: electrons of low velocity were sent out from the glowing wire D (Fig 65). Between D and the net-like electrode N was a variable electric field by which the electrons were accelerated. Between N and the collecting electrode G was a field of a properly chosen (constant) opposing potential, which up to a certain degree retarded the electrons again, so that only those electrons which possessed velocities exceeding a certain value at *N* could reach *G*. The number which actually reached *G* was established by measuring the negative current flowing from *G* by means of a galvanometer. A series of values observed by Franck and Hertz, with mercury vapor as the gas, is represented in Fig. 66, in which the negative current flowing through the galvanometer, *i.e.*, the number of electrons reaching *G*, is plotted as a function of the accelerating potential between *D* and *N*, *i.e.*, as the total acceleration given to the electrons between *D* and *N*. The figure indicates the following points: if the accelerating potential is less than the opposing potential (in the figure, about 2 *volts*), no electrons reach the collecting electrode. Current flows as soon as electrons become so strongly accelerated that they can overcome the opposing potential. By further increasing the potential up to about 4.9 *volts* the current suddenly decreases to zero. This signifies that the electrons have lost their velocity in the vicinity of the netting *N* by inelastic collisions with mercury atoms and can no longer move against the opposing potential. If the potential is raised still more, then the zone in which the electrons lose their velocities again moves suddenly back towards *D*. They thus still have a certain distance to pass before the netting *N* is reached, so that again, under the proper conditions, they can attain a velocity which will allow them to reach *G*.

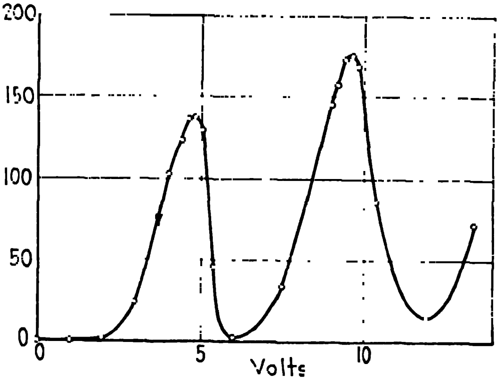

FIG 66

At about 9.8, or 2 × 4.9, *volts*, they for the second time reach the limiting velocity, which they again lose completely by collision with the mercury atoms, so that the current once more sinks to zero, etc.

It is remarkable that the curve, and especially the value of the limiting potential 4.9 *volts*, is practically independent of the gas pressure. In general, the electron on its way between *D* and *N* does not travel on a straight line but follows a zigzag path, due to collisions. If these collisions were inelastic, the energy would, of course, be consumed, *i.e.*, at high gas pressures the electrons would reach *N* with a lower velocity than if the pressure were low. The independence of the limiting potential, 4.9 *volts*, with respect to the gas pressure, therefore, proves that the collisions really are elastic.

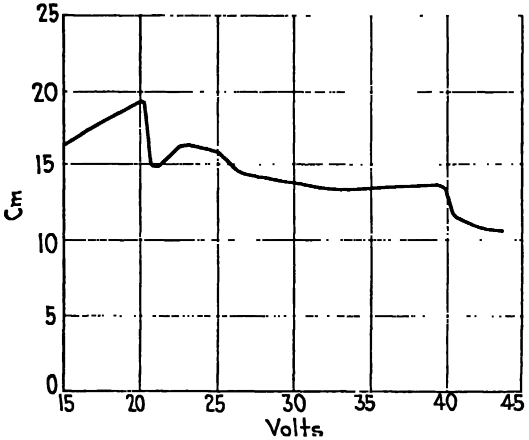

Fig 67

In case the electron is accelerated above the limiting velocity at the first inelastic collision that follows, a greater amount of energy will be absorbed by the atom, but this amount is likewise not continuous but changes in sudden jumps. Proof of this fact is found in the curve in Fig. 67, which was obtained with helium at a low pressure. The first time the current strength decreases rapidly is at about 20.5 *volts*; therefore the first inelastic collisions occur at this point. (The electronic energy required for this purpose by the noble gas, helium, is considerably greater than that required by the relatively reactive mercury atom!) A second, although less definite, decrease is shown at about 25 *volts*. At this point those electrons which previously had not accidentally struck gas molecules lose their velocities suddenly. It would not be possible to understand this break in the curve if we did not have at this point another sort of collision, in which the electron suddenly lost its total velocity (25 *volts*). The break at 40 *volts* corresponds to the repetition of the one at 20.5 *volts*, as has already been explained.

However, the assumption that the so-called" stable" paths of the electron are to be the only possible ones involves logical difficulties and contradictions with experience. For example, in the scattering of light by atoms (dispersion), a transient, non-quantum-like absorption of energy by the atoms takes place without doubt, and it is well explained by the classical electromagnetic laws. All the phenomena are nicely accounted for if it is assumed that the electron really can move in orbits located between the "stable" ones, but that under these circumstances it radiates and therefore strives very rapidly to reach one of the stable orbits in which no radiation occurs. Probably the electron always goes spontaneously from a labile, "transition" orbit to a deeper situated stable orbit in which it stays continuously, or at least for some time, without radiation. From a stable orbit the electron can be removed to a higher transition orbit by a temporary energy absorption, but, in general, returns immediately to the stable orbit as soon as the force acting on it ceases. Only when the total added energy is sufficient to raise the electron to a higher stable (or, more exactly, "quasistable") orbit will the atom retain the absorbed energy for a longer time.[1]

b. THE EINSTEIN-BOHR FREQUENCY LAW

297. Formulation of the Law.—In all atoms there exists a fundamental orbit in which the electron is stable continuously and which, in comparison with all other orbits, possesses a minimum energy. In the remaining "quasistable" orbits, the electron is, of course, able to stay for a time but not continuously. Just as in the radioactive disintegration, it appears as if after a very short time (usually), a sort of "life period," a spontaneous transition to a deeper orbit or to the fundamental orbit occurs. In this case the electron must give up energy; if the atom is isolated and no direct, mechanical energy transference is involved, *the emission of an electromagnetic wave offers the only possibility of liberating energy*

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[1] * Only one of the various possibilities is discussed in the text This problem of optical dispersion has recently been attacked by Bohr, Kramers and Slater (*Phil. Mag*, **47,** 785 (1924)). The assumption of intermediate transition orbits was not found necessary for the solution but radical assumptions concerning the validity of the First Law were involved See also the notes by Kramers in *Nature,* **113,** 673; **114,** 310 (1924).

The transformation of atomic energy into radiant energy resulting from the transition of an electron is governed by a fundamental and quite characteristic law, according to which the frequency of the emitted electromagnetic wave depends on nothing but the energy difference $U_1 - U_2$ of the two orbits, we have

$$h\nu = U_1 - U_2, \tag{267}$$

in which the proportionality factor h is a universal constant which has already been introduced in **74** as **Planck's elementary quantum of action.**[1]

The law was first announced by Einstein (1905) and applied to the photoelectric and other related phenomena. Later it was extended by Bohr (1913) to other processes, especially to the emission of spectral lines.

Equation (267) holds not only for the transformation of atomic energy into radiant energy (the emission process), but also for the reverse process of energy absorption. In this case Eq. (267) means: if a radiation of a definite frequency ν acts upon an atom, energy can be absorbed continuously only if an electron can increase its orbital energy by exactly $U_1 - U_2 = h\nu$, i e , if $U_1 - U_2$ corresponds to the jump of an electron from one "stable" orbit to another. Thus, if it is at all possible for the radiation to deliver energy continuously to the atom, *it takes place only in quanta of the magnitude hν.*

The frequency law (Äquivalentgesetz) makes no statements regarding the details of the mechanism by which the energy is transferred between radiant and atomic energy. In this respect it is analogous to the energy principle, which likewise says nothing further than that in their transformations from one form to another certain amounts of energy are equivalent. Thus the question of the details of the transformation are left completely open.

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[1] * An excellent presentation of the theory and applications of energy quanta to modern problems is given by REICHE, FRITZ, "The Quantum Theory," translated by HATFIELD and BROSE, E. P. Dutton & Company Numerous notes and references are given.

From the standpoint of the last statement of **296,** the frequency law states that from all labile orbits between two stable orbits the electron always emits one and the same frequency. Thus, according to the frequency law, we have as the characteristics of the whole intermediate state between the two stable orbits: (1) the frequency of the emitted radiation, and (2) the energy difference $U_1 - U_2$ between the two stable orbits.

It may be specially emphasized that Eq. (267) is valid for a so-called elementary process, *i.e.*, it holds for the energy change of a single atom or a single molecule

The complete removal of an electron and its return to the atom belong among those elementary processes for which Eq. (267) is directly applicable. According to Eq. (266) we get

$$h\nu = -U_2 = \frac{A'}{2a} \tag{267a}$$

or

$$h\nu = U_l + \frac{A'}{2a}, \tag{267b}$$

depending upon whether the electron at infinite distance from the kernel ($a = \infty$) is at rest or moving In the former case $U_1 = 0$; in the latter U_1 is equal to the kinetic energy of the electron outside of the atom U_k.

c. THE TRANSFORMATION OF THE KINETIC ENERGY OF THE ELECTRON INTO RADIANT ENERGY, AND VICE VERSA

298. The Production of X-rays.[1] Equation (267*b*) may first be applied to the production of radiant energy by rapidly moving electrons.

If an electron passes through a potential gradient of 10,000 to 100,000 *volts* and thus acquires a velocity (see Eq (258*a*)) of about $5.94 \cdot 10^7\sqrt{E} \simeq 0.6$ to $2 \cdot 10^{10}$ *cm./sec* U_k becomes rather large, and therefore, upon striking an atom in which it is absorbed, a radiation of very high frequency with a wave length of the order of magnitude $1 \cdot 10^{-8}$ *cm* (1Å.) will be emitted. This involves the emission of X-rays and a continuous X-ray spectrum (the "white" Rontgen light) is obtained if the electrons hit with different velocities Since in atoms or atom ions it is generally only the outer orbits, *i e*, with

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[1] * For a discussion of the practical details of X-ray production as well as a considerable amount of data see KAYE, "X-rays," 4th ed , Longmans, Green & Co (1923)

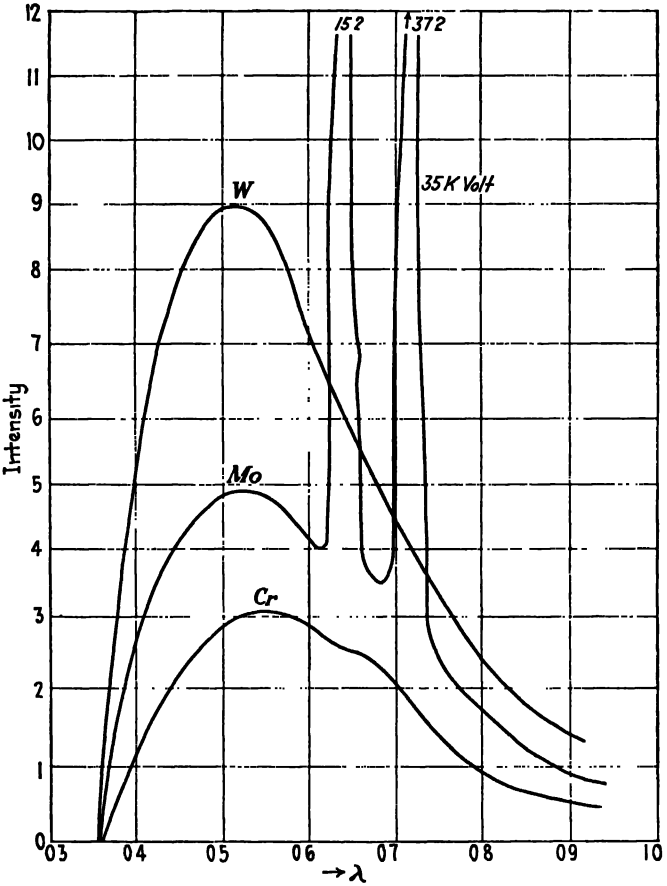

Fig 68

relatively great radii, which are unoccupied and therefore it is to these orbits that the electron can return directly, it is practical to disregard the energy term $\frac{A'}{2a}$ in comparison with U_k when the production of X-rays is being considered; for each wave length we have the expression

$$U_k = h\nu. \qquad (267c)$$

The kinetic energy U_k is now equal to Ee_0, where E represents the potential gradient through which the electron has passed. The greatest value which E can assume is the total potential difference E_0 between the two electrodes. Therefore, the kinetic energy has a maximum value which amounts to $U_{km} = E_0e_0$ From Eq. (267*c*), therefore, the frequency of the continuous spectrum must also have as its maximum value

$$\nu_m = \frac{E_0e_0}{h}, \tag{268}$$

at which the spectrum suddenly stops.

This conclusion has been confirmed by the experiments of various investigators. The approximate distribution of intensities among the various wave lengths of a continuous X-ray spectrum is shown in Fig 68, which is based upon observations by C T Ulrey. The X-rays were produced from various metals, using a potential of 35,000 volts, and the intensity of the rays after being resolved into a spectrum was measured by ionization The sharp disappearance of the continuous spectrum (on the left side of the diagram), and especially its independence of the kind of metal with which the electrons collided during the emission of the X-rays, are striking. (For molybdenum several bands of the line spectrum also appear)

Equation (268) can thus be used directly for determining the universal constant h The procedure is unusual in its simplicity We need only measure the direct-current potential E_0 across the X-ray tube (apart from small correction factors) and the wave length or rate of vibration of the limiting frequency at which the X-ray spectrum sharply disappears The methods most generally used for measuring the wave lengths of the X-rays are given in **322.** The values of h found by various investigators using this method vary between 6 53 (Wagner) and $6\ 557 \cdot 10^{-27}$ (Blake and Duane) and may be placed among the most accurate determinations of this constant of nature[1]

299. Application of the Frequency Law to the Photoelectric Effect.

—If Eq. (267*b*) is applied to the transformation of radiant energy into the kinetic energy of electrons, it requires that X-rays of a definite wave length liberate electrons with velocities differing by definite amounts (*i e*, discontinuously) from the atoms. This, of course, has been known for a long time in the production of the **secondary cathode rays** by illuminating solid bodies with the X-rays; quantitative measurements performed by de Broglie completely confirmed Eq. (267*b*).[2]

[1] Articles which summarize the material on this subject are: Wagner, E, *Jahr Radioakt Elektronik*, **16,** 190 (1919), Ladenburg, R, *ibid*, **17,** 93, 273 (1920), also the reprint, "Plancks elementares Wirkungsquantum usw," published by S Hirzel, Leipzig (1921) *Bragg, W H and W. L., "X-rays and Crystal Stucture," chap IV and VI, Bell, London (1924).

[2] *J. phys.* (6), **2,** 265 (1921).

Moreover, there are extensive observations on the liberation of electrons from metals, etc. by visible and ultra-violet light, a phenomenon which has already been described in **288** as the photoelectric effect. The energy quantum $h\nu$ in this case is about 1000 times smaller than with the X-rays, so that only the outermost electrons can be set free. However, according to **285**, the work $\frac{A'}{2a}$ required in separating electrons from solid metals consists much less in the work of freeing the electrons from the atomic union, since in the interior of the metal they are certainly very loosely bound, than in the work employed in bringing them through the surface.

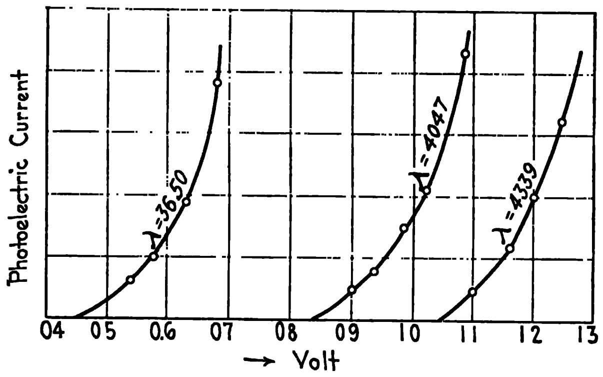

Fig 69.

The experimental proof of Eq (267*b*) is obtained by allowing monochromatic light of frequency ν to fall upon the metallic surface and measuring the velocity of the emerging electron. From this it is found that electrons with different velocities emerge when the surface is illuminated with a definite frequency, but that there exists a maximum velocity to which can be assigned a value which is more or less accurate, but seldom exceeded. When Eq (267*b*) is applied to the photoelectric effect, the term U_k signifies the kinetic energy of those electrons which emerge with this maximum velocity. The measurement of this quantity is made by surrounding the illuminated metal by a collecting electrode ("Faraday's cage") and applying a potential difference E_0 between it and the metal just sufficient to prevent any electrons from reaching the electrode For the kinetic energy of the most rapid electrons at the instant of their emergence we have $U_k = E_0 e_0$. The potential difference E_0 read directly upon the measuring instrument is generally not the effective difference E between the illuminated metal and the Faraday cage, and a correction must be introduced which becomes especially important when the potential differences are small. The disturbing factor is due to a "contact potential" K between the two different metals (cf. **371**). In place of Eq (267*b*) we obtain, therefore,

$$h\nu = (E_0 + K)e_0 + \frac{A'}{2a} \quad \text{or} \quad E_0 = \frac{h}{e_0}\nu - Const., \tag{269}$$

if $K + \frac{A'}{2ae_0}$ is considered as one constant.

Equation (269) is evaluated by measuring the values of the potential E_0, the **threshold potential,** at which the electrons just succeed in traveling from the metal to the cage for different monochromatic radiations. The transfer of electrons is indicated by a galvanometer against which the Faraday cage is earthed. Some observations by Millikan on lithium are reproduced in Fig 69, in which the current read on the galvanometer is represented as dependent upon the retarding potential and the relatively sharp appearance of the current at the definite potential is indicated. (E_0 is negative in these observations.)

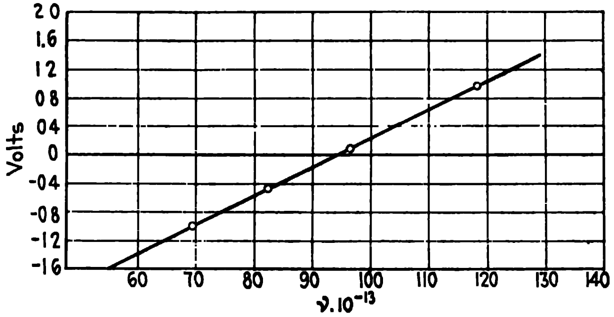

Fig. 70.

If the threshold values of the tension E_0 are expressed graphically as a function of the frequency ν of the incident radiation, a straight line is to be expected according to Eq (269). This requirement is fulfilled by the observed results as Fig. 70 shows. The slope of the straight line thus obtained must be independent of the nature of the illuminated metal and be equal to $\frac{h}{e_0}$ (cf. **4**). This expectation is also confirmed by the observations. The value of h found with various metals by various investigators from the slopes of such curves vary between $6.41 \cdot 10^{-27}$ (Al) and $6.58 \cdot 10^{-27}$ (Li).

d. PHOTOCHEMICAL PHENOMENA

300. General Photochemical Laws.—It is well known that light rays have an exceptionally marked influence on a number of chemical processes. The number of facts concerning such photochemical reactions is already very large, yet the majority of phenomena are so complicated that up to the present in only a few cases has an insight been obtained into the mechanism of the photochemical effect.[1] *In spite of this it can scarcely be doubted that the frequency law forms the basis for all photochemistry.* Before entering into the details of this law, several other general photochemical laws which may be considered as firmly established by experience will be briefly mentioned.

1. Only such rays as are absorbed by the system can possibly have a photochemical effect (Grotthus, 1817). It is not necessary, however, that the rays be absorbed by one of the reacting components; under certain circumstances a "sensitizer" which does not actually take part in the reaction can cause the absorption. For example, by the addition of a suitable red dye, photographic plates which react only to blue and other rays of short wave lengths can be made sensitive to red light also.

2. On the other hand, not all of the different kinds of rays which are absorbed are photochemically effective. Light of short wave lengths (ultra-violet) quite frequently has a photochemical effect, while light of long wave lengths (red) is quite often absorbed without exerting any chemical influence.

3. When secondary disturbances due to the products of reaction are avoided, the amount of substance changed by photochemical means is proportional to the product of the intensity of the photochemically active radiation and the time of illumination (Bunsen and Roscoe, 1862), *i.e.*, to the amount of radiant energy absorbed by the system.

301. Classification of Photochemical Reactions.—To discuss the existing material theoretically, it must first be classified in a suitable manner. Similar to ordinary chemical reactions the following may be differentiated:

1. Processes in which light acts catalytically; therefore, processes in which a reaction taking place normally in the dark may

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[1] Extensive discussions of photochemical phenomena are given by Weigert, F., "Die chemischen Wirkungen des Lichtes," Stuttgart (1911); Benrath, "Lehrbuch der Photochemie," Heidelberg (1912); Plotnikow, J., "Lehrbuch der allgemeinen Photochemie," Berlin (1920); *Lewis, W. McC., *loc. cit.*, vol. 2, chap. 14; vol 3, p. 134 *et seq;* Taylor, H. S., "Treatise on Physical Chemistry," *loc. cit.*, vol. 2, chap 18.

be either accelerated or retarded. (*Example:* The effect of light on the combination of H_2 and Cl_2 to form HCl.) It is clear that only a very small amount of radiant energy will be required for such a catalytic effect.

With light as with ordinary catalysts, specific effects can be observed, although not so often. Trautz[1] succeeded in showing that, while the oxidation of pyrogallol was retarded by ultraviolet light, it was accelerated by red light.

2. Reactions in which the equilibrium point reached by the chemical system under the influence of light is different from that reached in darkness. One of the most familiar examples of this sort of reaction is the reduction of carbonic acid in plants, which proceeds only in light. The polymerization of anthracene to dianthracene[2] represents an experimentally investigated case in which the displacement of the equilibrium during the illumination could be quantitatively followed. Of course, a considerably greater amount of radiant energy is generally required for the attainment of an observable displacement of the equilibrium than for a mere catalytic effect.

In order to apply the frequency law to photochemical reactions it is necessary, similar to the theory of reaction velocity of ordinary reactions, to resolve the observed gross reaction into a number of steps. Only one of these steps, usually the first, the **primary photochemical reaction,** is dependent upon the effect of light; the remaining steps, the **secondary reactions,** generally take place without any special peculiarities.

Various hypotheses have been advanced regarding the nature of the primary photochemical reaction. Warburg[3] and Nernst[4] assume that the primary reaction always consists of a diatomic molecule splitting into atoms. O. Stern and M. Volmer have shown[5] that it is more expedient to look upon the primary photochemical reaction as the transition of the molecule from the normal condition to one with a greater energy content and therefore to a more labile or reactive state.[1]

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[1] *Physik. Zeit.*, **7**, 899 (1906).

[2] LUTHER and WEIGERT, *Z physik. Chem.*, **51**, 297; **53**, 385 (1905); also TAYLOR, H A. and LEWIS, W Mc. C, *J. Am Chem Soc.*, **46**, 1606 (1924).

[3] *Berl Akad., Ber.*, p. 314 (1916), also *Z. Elektrochem.*, **26**, 54 (1920); **27**, 133 (1921).

[4] *Z. Elektrochem*, **24**, 335 (1918).

[5] *Z. wiss. Phot.*, **19**, 275 (1920).

Like the secondary reaction, an exchange between the molecules having a high energy content (designated by $[X]_b$) and the others is directly connected with the primary reaction. Perhaps in many cases the first secondary reaction involves a dissociation of the "energized" molecules into atoms, which then, in turn, enter into other combinations; yet, as a rule, the "energized" molecules appear to react directly with other molecules whether these be of the same or of different species.

302. Application of the Frequency Law to Primary Photochemical Reactions.—The amount of energy U_b which the molecules of the primary photochemical reaction absorbs from a radiation of frequency ν is given by Eq. (267):

$$U_b = h\nu. \tag{267}$$

This, then, represents a supply of energy at the disposal of the secondary reaction, which, in yellow light, amounts to about 50,000 *cal.* per mole; in violet light, to about 70,000 *cal.*, and in ultra-violet light of the wave length 2000 Å., up to 140,000 *cal.* From the magnitudes of these energy quantities it may be readily understood that a considerable number of reactions will be influenced by light, and without further remark it is seen that light of short wave lengths (ultra-violet) must, in general be, more active than that of long wave lengths (red).

A direct test of the frequency law in the form $U_b = h\nu$, such as by the establishment of a definite threshold value of ν at which an observable exchange begins, meets with difficulties on the following grounds: on the one hand, the amount of energy absorbed from the radiation is often not completely consumed in the promotion of the secondary reaction. If, for example, the energized molecule did not have the opportunity of reacting with another molecule for a certain period, or, in other words, if during this time some of its collisions were chemically ineffective, a part of the stored-up radiant energy would be lost without being chemically utilized.[1] On the other hand, the stored-up energy need not, under all conditions, be sufficient for the amount required by the secondary reaction.

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[1] Supporting this conception there is the remarkable fact that an amount of radiant energy can be added to certain diatomic molecules which is greater than the energy of dissociation, yet without resolving them into atoms. The I_2 molecule is an example of this. For a time it is able to absorb nearly double the amount of its dissociation energy and emit it again as fluorescence without dissociating (See STERN, OTTO and VOLMER, M., *Physik Zeit.*, **20**, 183 (1919).) According to the Nernst-Warburg hypothesis, all radiant energy absorbed above the dissociation energy must lead to dissociation.

In such cases the energy lacking can be taken from the heat motion of the molecules.[2]

However, in a number of cases it can be shown by other means that the fundamental assumption in Eq. (267), that energy is absorbed in quantum increments, is correct.

It may be assumed that the energy quantum absorbed by the primary reaction is greater than that required by the secondary. The individual molecule with which the primary reaction is concerned cannot absorb either more or less energy than the quantum $h\nu$, since energy cannot be further subdivided. In order to induce a primary reaction involving a definite number of molecules (N') and, accordingly, to induce the secondary reaction, the same number (N') of energy quanta is always necessary. The system must, therefore, remove an amount of energy $Q' = N'h\nu$ from the radiation, provided N' molecules are to be photochemically transformed. Thus,

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[1] The mean length of time during which the molecule remains in the energized state seems, as a rule, to be very short, of the order of 10^{-8} to 10^{-9} *sec.* (See Stern and Volmer, *loc. cit.*; also Noddack, W., *Z. Elektrochem.*, **27**, 359 (1921)). In other cases, however, it may attain very large values. The development of the latent image of a photographic plate and phosphorescence phenomena serve as examples of this.

[2] If, for example, the absorbed energy quantum is 70,000 *cal* per mole and the energy required by the secondary reaction only 100,000 *cal*, the heat motion needs only to exceed 30,000 *cal*; this is much easier to attain, and, accordingly, the reaction can take place at much lower temperatures than if the total heat of reaction of 100,000 *cal.* had to be suppplied by the heat motion.

Assume a reaction of the same type as the formation of water vapor, $2A_2 + B_2 = 2A_2B$. According to the approximation Eq. (239) for a heat of reaction of 100,000 *cal*, at $T = 300$ and $p = 1$ *atm*, it is found that the degree of dissociation is about 10^{-22} in darkness, while in light with a heat of reaction of 30,000 *cal.* it is about $10^{-4.6}$. This degree of dissociation must be reached as a limiting value under very intense illumination, provided the kind of ray involved (4000 Å) is actually photochemically effective for the particular reaction under consideration. The complete formula for the displacement of equilibrium by means of illumination may be found in an article by Einstein, A., *Ann. Physik.*, **37**, 832 (1912), or in Lewis, W. McC., *loc. cit.*, vol 3, p. 134.

$$N' = \frac{Q'}{h\nu}$$

or, expressed in moles,

$$n' = \frac{Q'}{\mathbf{N}h\nu}. \qquad (270)$$

Since Q', the total radiant energy absorbed during the reaction, ν, the mean frequency of the applied radiation, and n', the number of transformed molecules, can all be measured, this equation[1] can be subjected to experimental test.

Equation (270) appears on first sight to be paradoxical and in opposition to general experience, because it states that the amount of material transformed becomes smaller as the frequency increases. It is to be noted, however, that this equation is valid only if the threshold value $h\nu = U_l$, which is sufficient for the reaction, is exceeded. If ν rises above this threshold value, the energy quanta $h\nu$, each of which falls upon one molecule, will always become greater; thus a definite amount of available energy can only activate and transform a smaller number of molecules.

303. Experimental Tests of Eq. (270).—For testing Eq. (270), reactions were chosen as far as possible from those which showed a shifting of the point of equilibrium under illumination, because if light acted only as a catalytic agent there would exist the possibility that the primary reaction only took place with very few molecules and that some intermediate products within certain limits would account for the progress of the reaction. The total transformation in this case would be considerably greater than would be expected according to Eq. (270). As an example of such a case the combination of hydrogen and chlorine to form HCl may be mentioned. Considerably more HCl is usually formed than Eq. (270) accounts for, but what the intermediate products are cannot be established with certainty. Since the presence of water vapor (in traces) is absolutely essential for starting off the combination of these two gases by photochemical means, it may be supposed that the first secondary reaction is the combination of an activated Cl_2 molecule with a water molecule.

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[1] EINSTEIN, *Ann. Physik.* (4), **17**, 132 (1905); **37**, 832 (1912).

A carefully investigated photochemical reaction in which illumination shifts the equilibrium point is the decomposition of hydrogen iodide into its elements.[1]

$$HI \rightarrow \frac{1}{2}H_2 + \frac{1}{2}I_2.$$

It is assumed that the reaction takes place in the following steps:

$$HI \rightarrow [HI]_b \qquad \text{Primary reaction}$$
$$[HI]_b + HI \rightarrow H_2 + I_2 \qquad \text{Secondary reaction}$$

Through the absorption of one energy quantum by the primary reaction, a total of two molecules of HI is decomposed as the result of the corresponding secondary reaction. Therefore in this case the yield must be twice as great as given by Eq. (270).

Warburg's experimental results are collected in Table 73, in which the number of moles of $I_2(n')$ actually formed during the application of 1 *cal.* ($Q' = 1$) of radiant energy is compared with the doubled value as calculated from Eq. (270).

TABLE 73

Wave length of the light used (A.)	n' obs.	$n' = \frac{2}{\mathbf{N}h\nu}$
2070	1 44 10^{-5}	1 458 10^{-5}
2530	1 85 10^{-5}	1 781 10^{-5}
2820	2 08 · 10^{-5}	1 985 · 10^{-5}

The result represents a complete confirmation of the Einstein equation, and shows, in particular, that by the application of a definite amount of energy more molecules are actually decomposed when the wave length is longer, the corresponding quantum of radiant energy thus being smaller.

Equation (270) is confirmed equally well by the following reactions:

The conversion of oxygen to ozone by wave length 2000 Å.[2]

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[1] WARBURG, *Berl. Akad. Ber*, p. 1228 (1918).

[2] WARBURG, E., *Berl Akad. Ber.*, p. 644 (1913); p. 872 (1914).

The decomposition of hydrogen bromide into its elements.[1]
The reaction between bromine and hexahydrobenzol.[2]
The action of chlorine on trichlorbrommethane.[3]
The decomposition of solid silver bromide into its elements.[4]

There are, of course, a number of other reactions which do not exactly confirm this equation, yet in the majority of these cases it seems probable that the results are to be explained by means of secondary phenomena,[5] especially through the loss of energy by the activated molecule before the occurrence of a chemically effective collision. In this respect the above-mentioned action of chlorine on the trichlorbrommethane, investigated by Noddack, is instructive. If chlorine is dissolved in pure trichlorbrommethane, the Einstein law holds, but the more the solution is diluted with carbon tetrachloride the less becomes the actual exchange as compared with the amount calculated. Since dilution reduces the probability of a collision between an activated Cl_2 molecule and a $CBrCl_3$ molecule, these results indicate that an activated Cl_2 molecule without doubt exists in this state for only a limited time. The question of whether the molecule loses its energy spontaneously on the way, perhaps by an emission, or as the result of a collision with a CCl_4 molecule, must certainly remain open for the present.

e. ATOMIC SPECTRA

304. General.—It has already been mentioned in **262** that atoms are able to radiate spectra which consist of a number of discrete lines.

According to Bohr, each spectral line corresponds to an energy transition from one (quasi) stable state of the atom to another and thus depends upon the fundamental Eq. (267); since only a certain number of states (electronic orbits) are present, there is likewise only a limited number of possible energy transitions or spectral lines. Continuous spectra are obtained only when the electrons return to the atom from infinity with velocities which vary continuously. As a result of the highly developed methods of optical measurement, all the details of these line spectra can be determined very accurately, thus giving an insight into the inner processes of the atoms such as is furnished by no other physical or chemical phenomena.

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[1] WARBURG, E., *Berl Akad Ber*, p 314 (1916)

[2] PUSCH, LOTTE, *Z. Elektrochem*, **24,** 337 (1918)

[3] NODDACK, W., *Z Elektrochem*, **27,** 359 (1921).

[4] EGGERT, J, and NODDACK, W, *Berl. Akad Ber*, p 116 (1923).

[5] In the action of X-rays on photographic plates, one energy quantum is able to split up many thousands of AgBr molecules. Without doubt, this is a case where the primary absorbing atoms send out secondary cathode rays (**299**) through which a supplementary distribution of energy quanta is effected; in the case of X-rays this energy is quite large.

a The Means of Exciting the Emission of Spectral Lines from Atoms

305. Excitation by Means of Absorption.—At ordinary temperatures the atoms generally exist in a normal state in which the electrons describe their fundamental orbits which are distinguished by a minimum of potential energy. An emission of spectral lines associated with an energy change according to Eq (267) is, therefore, impossible; in order that such an emission can occur, at least *one* electron must first be "raised" to a more distant orbit by an addition of energy or, as it is customarily expressed, the atom must be "*excited.*" Now when an electron returns from a more distant orbit to the fundamental one or jumps into one of the intermediate, quasistable orbits, a spectral line is emitted whose frequency, according to Eq. (267), corresponds to the energy difference of the two orbits.

The energy necessary to raise the electron from the normal to a more distant orbit can be imparted to the atom in various ways.

First, the energy taken up by the atom can be supplied by the absorption of radiant energy. Since the atom is able to remove only definite energy quanta $\epsilon_1, \epsilon_2, \epsilon_3, \ldots$ from its surroundings (the *field of radiation*) on account of the limited number of stable electronic orbits, it will not absorb all the radiation equally but only a limited number of sharp spectral lines; this follows from Eq. (267). Continuous absorption is obtained only when the impinging energy quantum is greater than is necessary to raise the electron to the outermost orbit, *i.e.*, when the electron is not only completely removed from the atom but is emitted with a certain additional kinetic energy U_k. This has been demonstrated for a number of atoms in certain regions of the X-rays as well as in the visible and ultra-violet portions of the spectrum.

Conversely, if an electron returning to an atom strikes an atom ion with a certain kinetic energy U_k and at once reaches the orbit of the normal state, then an emission of a radiation is to be expected whose frequency number is defined by Eq. (267*b*) as $h\nu = U_k + \frac{A'}{2a_0}$, in which $\frac{A'}{2a_0}$ is the energy of the normal orbit. Since U_k varies continuously, a continuous spectrum which lies above the frequency ν_∞ corresponding to $U_1 - U_2 = 0 + \frac{A'}{2a_0}$ must accordingly be liberated under certain conditions. This continuous emission spectrum is completely analogous to the continuous absorption spectrum. (*Cf.* **292.**)

At the present time we do not possess a more accurate conception of how the transformation of radiant energy into atomic energy proceeds. At any rate it may be said to be very probable that the act of emission or absorption (because of passing through a number of labile transition orbits) does not take place instantaneously but within a finite time. In favor of this is the fact that spectral lines exist which are still able to show interference up to the path differences of about 1 *m*.

306. Stokes' Law.—Sometimes the radiant energy absorbed by a system is again emitted either at once or after some time in the form of radiation, *i.e.*, light. If liberated at once, the phenomenon is called **fluorescence**; if later, **phosphorescence.**[1]

It may be assumed that the atom has taken up the energy $\epsilon = h\nu_0$ by absorption, *i.e.*, has absorbed a line ν_0. In case the electron returns directly from the excited state back to its normal state, the frequency of the emitted light will be given simply by $\nu_e = \nu_0$; in other words, the fluorescent light has the same frequency as the light which excites it. But the electron often proceeds back to the normal state over various intermediate steps, in which case $h\nu_0 > h\nu_e$ or $\lambda_e > \lambda_0$ must be true.

The frequency law thus explains an old rule first expressed by Stokes (1852), which stated that the fluorescent and phosphorescent light emitted was, in general, of a longer wave length than the absorbed (exciting) light.

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[1] P. Pringsheim has a summary of the extensive material on this subject in his monograph, "Fluoreszenz und Phosphoreszenz," 2nd ed., Berlin (1923).

The exceptions to Stokes' rule which have been observed from time to time are theoretically possible, since the energy necessary to raise an electron to an outer orbit does not correspond to a single energy quantum but might be a combination of several different amounts such as several quanta absorbed successively $h\nu_0 + h\nu_1$ . . . Under certain circumstances energy can flow into the atom from another source, such as from a collision with another atom, simultaneously with the absorption of a quantum $h\nu_0$ from the radiation. In such cases, therefore, there is a larger energy quantum available for emission than would be taken up by the absorption of the frequency ν_0 alone and the result would then be $\nu_0 < \nu_c$.

307. Excitation of the Atoms by Molecular Collision.—A second way in which the atom can obtain the energy necessary for its excitation is by collision with other atoms or molecules. Since the molecular energy increases as the temperature rises, it is evident that the number of transitions from the normal to the excited state, and therefore also the number of atoms returning to the normal state or, in other words, the intensity of the emitted radiation, can be very much increased by raising the temperature. To be sure, the mean kinetic energy of the molecules, even at relatively high temperatures, is too small to raise the electron to an orbit from which the energy difference $U_1 - U_2$ ($= h\nu$) compared with the normal state corresponds to a vibration lying within the range of visible light. However, as a result of Maxwell's law of distribution of velocities, molecules are found in every gas with velocities considerably greater than the mean value, so that sufficient energy is available to excite an atom, especially if it undergoes several collisions.

For example, in order to excite a line in the visible region of the spectrum of about 5000 Å. $= 5 \cdot 10^{-5}$ *cm.* corresponding to a single jump in the normal orbit, energy amounting to at least $h\nu = \dfrac{6.55 \times 10^{-27} \times 3 \times 10^{10}}{5 \times 10^{-5}} \simeq 4 \cdot 10^{-12}$ *ergs* is required. Now let the mean kinetic energy of a molecule be expressed directly as a function of the temperature (Eq. (84)) $U_k = \frac{3}{2}kT = \frac{3}{2} \times 1.37 \times 10^{-16}T$ *ergs*. A single molecule must, therefore, possess energy corresponding to a temperature of $T = \dfrac{4 \times 10^{-12}}{\frac{3}{2} \times 1.37 \times 10^{-16}}$

$\simeq$ 20,000° before the collision takes place, in order to be able to excite an atom in the manner described. Now the calculation according to Maxwell's law indicates that

WHEN THE MEAN ABSOLUTE TEMPERATURE OF THE GAS IS	THE FRACTION OF INDIVIDUAL MOLECULES, EACH OF WHICH HAS KINETIC ENERGY OF AT LEAST 4 10^{12} *ergs*, IS
500°	7 1 10^{-22}
1000°	5 7 10^{-11}
2000°	1 35 10^{-6}
5000°	7 5 10^{-3}

Thus, if one mole of a gas is considered, then in the time in which a rapid molecule travels over its mean free path only $6.06 \times 10^{23} \times 7 \times 10^{-22}$ approx. 400 atoms will be brought into the excited state at $T = 500°$; but, of these, usually only a part will lose their energy quanta by radiation, while the remainder return directly to the normal state as the result of molecular collision. Therefore, as far as radiation at 500° *abs.* is concerned, so few atoms are actually effective that a luminosity of the gas is not apparent. This agrees with experience. However, the number of atoms excited in a definite time increases so rapidly with increasing temperature that the beginning of luminosity at a somewhat sharply definable temperature can be readily understood. For atoms which actually radiate visible light by the return of an electron to the normal state (*e g* , in a number of metallic vapors) this temperature is about 800° *abs.* It follows that only relatively few of the atoms of luminous gases are able to take part in the emission of light at the same time—at least if the period of emission of a single atom is regarded as being relatively short. For hydrogen, oxygen, and nitrogen the beginning of luminescence lies at a very much higher temperature than for the metallic vapors, one reason being that these substances form diatomic molecules at low temperatures, and another that a greater amount of energy is required to excite the atom out of its normal state than corresponds to a radiation of visible light (*cf.* **310**).

308. Excitation by Means of Collisions with Electrons.—The excitation of atoms by collision with electrons is of particular interest. When electrons are caused to travel through a definite difference of electrical potential, it is possible to determine accurately the energy added to the atom and to test if definite exciting energies result in single spectral ranges as is to be expected from Eq. (267).

Franck and Hertz (1914) first succeeded in showing that gaseous mercury atoms struck by electrons suddenly began to emit the mercury line 2536.7 Å. when the potential gradient which the electron passed through amounted to 4.9 *volts*. This is exactly the same potential at which the first inelastic collision occurs (*cf.* **296**). Thus, the total energy given up by the "4.9-*volt* electron" is completely consumed in the removal of the electron from the normal orbit of the atom to another orbit from which the electron, in returning to the normal state, emits the line 2536.7 A. Equation (267) is therefore again found to be quite accurately confirmed; for the energy quantum of line 2536.7 A. we have

$$h\nu = \frac{6.55 \times 10^{-27} \times 3 \times 10^{10}}{25367 \times 10^{-9}} = 7.74 \cdot 10^{-12}\ ergs,$$

while the energy of a "4.9-*volt* electron" in absolute units is

$$1.59 \times 10^{-20} \times 4.9 \times 10^{8} = 7.8 \cdot 10^{-12}\ ergs.$$

The same effect was later demonstrated for a number of other substances, in particular the noble gases, ordinary diatomic gases, and metal vapors. *The potential through which the electron must pass in order to cause the first inelastic collision with the atom and to excite the emission of a spectral line is called the* **resonance potential.**[1]

If the resonance potential is relatively high, as in the noble gases, the emitted line lies among the short wave lengths of the ultra-violet portion These wave lengths are most readily detected by means of their photoelectric effect (see **288**). The apparatus already described in **296** can be used The emitted radiation is collected upon the electrode *G* (Fig 65) from which electrons are thus liberated and thrown out with a low velocity. If the electrons are prevented from traveling from *D* to *G* by placing a suitably strong opposing field between *G* and *N*, then *G* can become positively charged only as the result of the photoelectrically liberated electrons, *i e*, a positive current flows through the galvonometer The observations agree completely with these considerations If the accelerating potential acting on the electrons is gradually increased, the galvanometer first shows an appreciable movement when the resonance potential is reached, *i e*, at the moment when the first resonance line is emitted Upon increasing the potential still further, the photoelectric current remains nearly constant for a time and later increases suddenly at a definite potential. This discontinuous increase which under certain circumstances may repeat[1] itself a number of times is explained as follows: upon reaching the resonance potential the line corresponding to it is emitted for the first time If the electrons are accelerated above this resonance potential, they will emit no new line until the energy of the impinging electron becomes sufficient to remove one of the electrons of the atom from the normal orbit to a second orbit; a new line of shorter wave length is then suddenly emitted The discontinuous increase of the photoelectric current at several potentials is thus a result of the emission of new spectral lines which suddenly appear at particular points. As was mentioned above, the resonance potential indicated by the first occurrence of a galvanometer movement is associated with the appearance of a quite definite spectral line and in the same way the other observed breaks on the photoelectric curve are also to be associated with definite spectral lines.

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[1] * In this case one of the outer electrons is merely *forced into another orbit* of higher energy content. Compare with the definition of ionization potential.

If the wave length of the corresponding spectral line is calculated from the potential E_k at the break ($e_0E_k = h\nu$), it is found to agree in most cases with a well-known spectral line, and, indeed, the agreement between the observed and the calculated lines concerned in these cases is so satisfactory that it is possible to determine the value of the universal constant h quite accurately from the values of E_k and ν. This procedure gives, as an average value, $h = 6.58 \cdot 10^{-27}$, which is in good agreement with the values found by the other methods.

Finally, if the potential is increased still further, the point is reached at which an electron is removed to an infinite distance from its normal orbit. *The potential difference through which the colliding electron must pass in order to obtain the energy required for this purpose is called the* **ionization potential.** Thus, this is a direct measurement of the work of separating an electron from its normal state. Since above the ionization potential the electric current flowing from the collecting electrode G is produced not only by the electrons sent out photoelectrically but also by the positive ions (produced by the liberation of electrons) striking the electrode, the break corresponding to the ionization potential is particularly well defined.[2]

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[1] Franck, J. and Einsporn, E, *Z Physik.*, **2**, 18 (1920); * see also Davis and Goucher, *Phys. Rev.*, **13**, 1 (1919)

[2] J. Franck discusses a large number of the more recent investigations of the excitation of light by electron impact, and of ionization potentials, in *Physik. Zeit.*, **22**, 388, 409, 441, 466 (1921). * See also Foote and Mohler, *loc. cit*, chap. III, and p. 149.

β The Hydrogen Spectrum

309. Empirical Relations.—In order to appreciate better the laws which hold for the various electron orbits and which were found from the spectral phenomena, we shall begin with a consideration of the simplest atom, hydrogen, which, according to **291**, consists of a singly charged positive nucleus with a single electron revolving about it.

Experience shows that the spectral lines emitted by hydrogen, as well as numerous other elements, can be combined into several "series," whose wave lengths and frequency numbers are given in an abbreviated form in the following table:

TABLE 74.—SOME SPECTRAL LINES FROM HYDROGEN

Series	Wave length obs (vacuum)	ν' obs	n	m	ν' calc from (271 $a - c$)	Remarks
Infra-red (Paschen) series	18751 3 Å	5332 96	3	4	5331 56	Name of line:
	12817 5	7801 83	3	5	7799 30	
Balmer series (partly in the visible region)	6564 66	15233 08	2	3	15233 01	Hα
	4862 71	20564 65	2	4	20561 57	Hβ
	4341 71	23032 41	2	5	23032 31	Hγ
	4102 91	24372 93	2	6	24372 82	Hδ
	3971 20	25181 13	2	7	25181 10	Besides a number of other lines up to m = 30, a part of which have been found only in stellar spectra
	3799 00	26322 72	2	10	26322 64	
	3712 70	26934 54	2	15	26931 97	
			2	∞	27419 42	
Lyman series (ultra-violet)	1216	82236	1	2	82258 27	
	1026	97465	1	3	97491 28	
	972	102880	1	4	102822 84	
			1	∞	109677.69	

In Fig. 71, the Balmer series is graphically represented, this series being typical also for other line spectra: towards the long wave-length end of the spectrum (small frequency numbers) the distance between individual lines is large; towards the short wave-length end they draw closer and closer together; at a very definite point (**the head of the series**) the line spectrum ceases. (The continuous spectrum mentioned in **305** is also connected with this point.)

By means of the following empirical formula, Balmer (1885) was able to reproduce the wave lengths of the hydrogen lines lying in the visible region with great accuracy:

$$\lambda = 3645.6\frac{m^2}{m^2 - 4}, \tag{271}$$

in which m can assume the value 3, 4, 5, 6, . . .

Written in another form, Eq. (271) becomes

$$\frac{1}{\lambda} = \nu' = \Re\left(\frac{1}{2^2} - \frac{1}{m^2}\right)(m = 3, 4, 5, 6 \quad . \ .), \tag{271a}$$

if ν' is the reciprocal of the wave length, the so-called **wave number,** *i.e.*, the number of waves (measured in vacuum) occurring in a path 1 *cm.* long.[1]

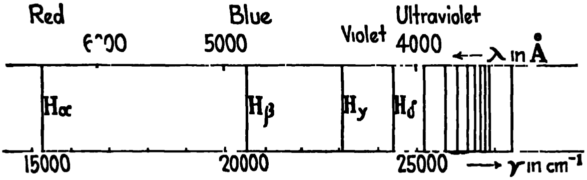

FIG 71.

The constant $\Re$, the **Rydberg constant,** has the value 109677.69 for hydrogen. The first term $\frac{1}{2^2}$ gives the head of the series, since for $m = \infty$ the second term vanishes. The Paschen series may be brought into the same form as the Balmer series:

$$\nu' = \Re\left(\frac{1}{3^2} - \frac{1}{m^2}\right)(m = 4, 5, 6 \quad . \ .). \tag{271b}$$

Finally for the Lyman series we have

$$\nu' = \Re\left(\frac{1}{1} - \frac{1}{m^2}\right)(m = 2, 3, 4 \qquad). \tag{271c}$$

310. The Energy Differences between Various Electronic Orbits.—The relationship between Eqs. (271*a, b, c*) and (267) is readily seen. If they are combined, the denominator of the first member being represented by n^2 and the result then multiplied by hV_l, we obtain

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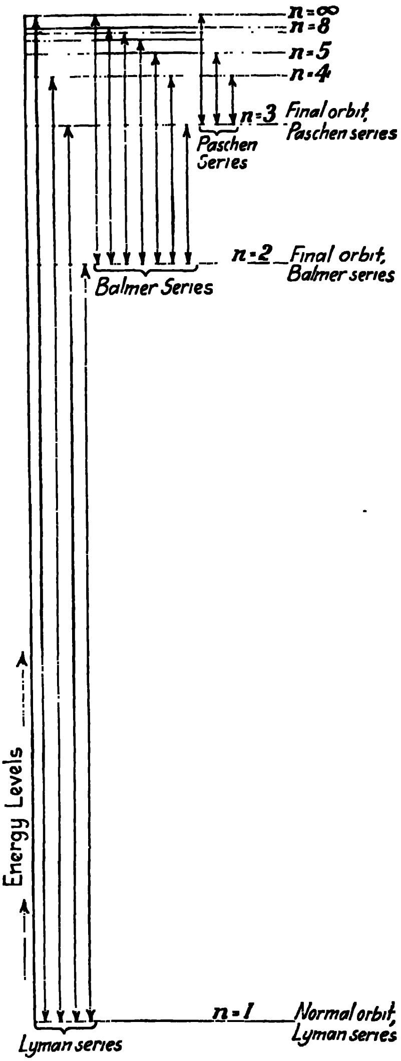
[1] The true frequency ν is greater than the wave number by a factor equal to the velocity of light: $\nu = V_l\nu'$.

$$\underbrace{h\nu = h\nu' V_l = \frac{\mathfrak{R} h V_l}{n^2} - \frac{\mathfrak{R} h V_l}{m^2}}$$

$$n = 1, 2, 3 \ . \ .$$

$$(m > n = 2, 3, 4, 5, 6). \qquad (271d)$$



n=∞
n=8
n=5
n=4
n=3 Final orbit, Paschen series
Paschen Series
n=2 Final orbit, Balmer series
Balmer Series
Energy Levels
n=1 Normal orbit, Lyman series
Lyman series

Fig. 72

The number m is variable and is called the **current number.** It distinguishes the individual successive members of the series from each other. The constant number n varies from series to series but is a constant for each series. Since we are concerned with two electronic orbits, the term $-\frac{\mathfrak{R} h V_l}{n^2}$ evidently corresponds to the energy U_2 of the one nearer to the nucleus, while $-\frac{\mathfrak{R} h V_l}{m^2}$ corresponds to the energy U_1 of the more distant orbit. In general, therefore, the energy of the electrons in the nth orbit is

$$U_n = -\frac{\mathfrak{R} h V_l}{n^2}, \qquad (272)$$

if the calculation starts at the normal orbit where $n = 1$. We can best appreciate the energy relations in the H atom by means of Fig. 72, which illustrates the magnitude of the energy differences between the various orbits. *The energy which is necessary to remove the electron to an infinite distance ($m = \infty$) from the normal orbit ($n = 1$), and which is equivalent to the work of ioniza-*

tion I **(308)**, *gives the limit or "head" of the series for the short wave lengths* ($h\nu V_l = I$). Just as the wave length of the first spectral line can be calculated from the resonance potential, the ionization potential gives the limit of the series (Lyman series) which is emitted when the electron returns to the normal state from an infinite distance.

311. Bohr's Model of the H Atom.—Niels Bohr has discussed the question of the physical conditions which determine the positions of the various stable orbits which the electrons describe without radiating.[1] It may first be assumed that the electrons move only in circles around the nucleus. Bohr's fundamental assumptions may be formulated as follows: in each stable orbit the kinetic energy U_k is equal to a whole number times an energy quantum of the value $\frac{h\mu}{2}$, where μ is the "frequency" of the electron in its orbit which varies for different orbits and which is connected with the angular velocity (ω) by the formula $2\pi\mu = \omega$. Thus:

$$U_k = \frac{nh\mu}{2} \quad (n = 1, 2, 3 \quad . \quad). \tag{273}$$

On the other hand we have for the kinetic energy of the electron which revolves on a circular path with the radius a (see **296**) the relation $U_k = \frac{1}{2}\frac{e_0^2}{a}$; since in this case $e_k = e_0$, we get:

$$U_k = \frac{m_0}{2}V^2 = \frac{m_0}{2}a^2\omega^2.$$

Finally we have

$$\frac{e_0^2}{2a} = \frac{m_0}{2}a^2\omega^2 = \frac{nh\omega}{4\pi}. \tag{274}$$

If we eliminate ω in one case and a in another, we find that the characteristic conditions for stable electronic orbits are given by

$$a = \frac{n^2h^2}{4\pi^2 m_0 e_0^2} \tag{275}$$

$$\omega = \frac{8\pi^3 m_0 e_0^4}{n^3h^3}. \tag{276}$$

The distance between the electronic orbits thus increases proportionally to the square of the whole numbers 1, 2, 3, 4, . ;

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[1] *Phil. Mag.*, **26**, 1 (1913). A general summary will be found in BOHR, "The Theory of Spectra and Atomic Constitution," Cambridge (1922).

the angular velocity varies inversely as the cube. If n is eliminated from Eqs. (275) and (276) it follows that

$$a^3 \omega^2 = \frac{e_0^2}{m_0} = Const., \tag{276a}$$

a relation which shows that Kepler's third law is valid also for electronic orbits.

The total energy of the electron in the nth orbit amounts to

$$U_n = U_p + U_k = -\frac{e_0^2}{a} + \frac{1}{2}\frac{e_0^2}{a} = -\frac{2\pi^2 m_0 e_0^4}{h^2 n^2}. \tag{277}$$

If this equation is compared with Eq. (272), then the Rydberg constant must be

$$\Re = \frac{2\pi^2 m_0 e_0^4}{h^3 V_l} = \frac{2\pi^2 e_0^5}{h^3 V_l}\left(\frac{m_0}{e_0}\right). \tag{278}$$

This expectation has, indeed, been confirmed and is one of the greatest results of the Bohr theory. By introducing into Eq. (278) the experimental values for $e_0 = 4.77 \cdot 10^{-10}$; $\frac{e_0}{m_0} = 5.31 \cdot 10^{17}$; $V_l = 3 \cdot 10^{10}$; $h = 6.55 \cdot 10^{-27}$, it is found that $\Re = 1.0950 \cdot 10^5$, which is in satisfactory agreement with the values found by optical methods.

It has been proved repeatedly that the frequency ν of the radiation emitted by an atom is determined only by the condition that $h\nu = U_1 - U_2$ and, in general, it is not at all the same as the orbital frequency of the electron $\mu = 2\pi\omega$.

For high values of n and m, *i.e.*, jumps between orbits, which are very far from the nucleus but still "within" the atom, ν and μ approach closer and closer. From Eq. (271*d*) we obtain

$$\nu' = \Re\left(\frac{1}{n^2} - \frac{1}{m^2}\right) = \Re\left(\frac{(m+n)(m-n)}{m^2 n^2}\right).$$

In case m and n are large numbers and differ only by 1, the percentage difference between them becomes very small, so that it can be written approximately that

$$\nu' = \Re\frac{2}{n^3}; \qquad \nu = \Re V_l \frac{2}{n^3}.$$

Taking Eqs. (278) and (276) into consideration, we obtain finally:

$$\nu = \frac{4\pi^2 m_0 e_0^4}{h^3 n^3} = \frac{\omega}{2\pi} = \mu.$$

Thus, *for the transition between two neighboring orbits which are at a large distance from the nucleus* (therefore possessing slow velocities of revolution) *the orbital frequency μ and the frequency ν of the emitted wave become equal.* Since this equality between the orbital frequency and the frequency of the emitted wave is characteristic of the classical theory (**295**) which is valid for macroscopic processes, the transition from quantum laws to classical laws is accomplished, and thus one of the most important fundamental requirements of the theory as a whole is fulfilled.

312. The Motion of the Nucleus.—For the preceding calculation of the energies of the electronic orbits, it was tacitly assumed that the mass of the nucleus is infinitely great compared with that of the electron and that, therefore, the center of gravity of the whole system coincided with the nucleus As a matter of fact, this assumption is not quite correct The nucleus and the electron actually move about their *common* center of gravity similar to the sun and the earth In other words, the nucleus also performs certain motions and therefore possesses both kinetic and potential energy referred to the common center of gravity. In view of this, the formula for the Rydberg constant $\mathfrak{R}_M$ for an atom with an atomic weight M is found to be

$$\mathfrak{R}_M = \frac{2\pi^2 m_0 e_0^4}{h^3 \mathrm{V}_l\left(1 + \frac{M_0}{M}\right)} = \frac{\mathfrak{R}_\infty}{1 + \frac{M_0}{M}}, \tag{278a}$$

instead of Eq (278) $\mathfrak{R}_\infty$ represents the extrapolated limit of the Rydberg constant and corresponds to the constant for an infinitely heavy atom; $\mathrm{N}m_0$ is replaced by M_0

Equation (278*a*) has been completely confirmed by experiment. Rydberg's constant is involved not only in the formula for the line spectrum of hydrogen but also in the formula for all other line spectra. Optical measurements indicate a small change in the Rydberg constant with the atomic weight; this change is greatest between hydrogen and helium, for which the optically determined ratio is

$$\frac{\mathfrak{R}_H}{\mathfrak{R}_{He}} = \frac{109677\ 691}{109722\ 144} = 0.999597,$$

while the ratio to be expected from Eq (278*a*) is

$$\frac{1 + \frac{1}{1850 \cdot 4}}{1 + \frac{1}{1850}} = 0.999593.$$

By means of Eq (278*a*) the value R_∞ = 109737 11 is obtained as the mean value for all the observations available at the present. This number is one of the most accurately determined constants of nature Therefore this equation can be used to calculate the values of the other constants m_0, e_0, or h appearing in it If $\frac{e_0}{m_0} = 1.765 \cdot 10^7$ and $e_0 = 4.774 \cdot 10^{-10}$ then $h =$

$6.545 \cdot 10^{-27}$, a number which at the present time represents the most accurate value of Planck's elementary quantum of action.[1]

313. Elliptical Orbits.—For what is to follow, especially for the problem of the electron configuration in the atoms above hydrogen, it is necessary to consider under what conditions elliptical orbits, as in the motion of planets, will also occur.

It is obvious from the previous discussion that to every circular orbit which is stable or quasistable according to the quantum condition Eq. (273) *a number of elliptical orbits can be assigned such that all those which have the same period of rotation and therefore the same frequency as the circular orbit are grouped together.*

The following propositions now result:

1. Since, according to Kepler's third law (Eq. (276)), which holds for electronic orbits also, the square of the period of revolution varies as the cube of the major axis or of the diameter of the circular orbit, *the major axes of all elliptical electron orbits which correspond to a definite period of revolution* τ *are the same and are equal to the diameter of the circular orbit of the same period.*

2. *The electron moving on an elliptical orbit has the same energy as an electron moving on the corresponding circular orbit.* As an exhaustive calculation shows, the total orbital energy (the sum of the kinetic and potential energy) in an ellipse depends only upon the magnitude of the major axis; thus Eq (277) still holds, but a becomes half the major axis of the ellipse instead of the radius of the circle

Since the frequency law states that the frequencies of the emitted spectral lines depend only upon the energies of the various orbits, *Eqs.* (271*a*) *and* (278) *hold rigorously for elliptical orbits also.* Thus a distinction between elliptical and circular orbits cannot be made by the spectral analysis, but this presupposes that the assumptions upon which this result is based are exactly fulfilled.

314. Perihelial Rotation or Precession of the Elliptical Orbits.—A fundamental change occurs if other forces are superimposed

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[1] * The term h has the dimensions (L^2MT^{-1}) of a moment of momentum. In general dynamics, such a quantity is called an "action" from the "principle of least action" in which it appears

$$[\text{Action}] = [\text{Energy} \times \text{Time.}]$$

(See Andrade, *loc cit.*, p 141.)

upon the force obeying Coulomb's law and proceeding from the point center (nucleus), even though the perturbing force is small. Since such disturbances are always present in the atom, their nature must be considered in some detail. As is well known, similar disturbances, the so-called "secular perturbations," occur even in astronomy, due to forces superimposed upon the simple Newtonian law which also refers to a point center (of mass).

It may first be assumed that the force of attraction proceeds only from the nucleus but that, besides the force which obeys Coulomb's law, there is another force varying in a different way with distance. For example, suppose that the equations for central motion, which hold for a rigorous quadratic relation between force and distance, are modified by a relativity change of mass with velocity,[1] which, at least approximately, can be formally represented by the addition of another force proportional to the reciprocal of the distance cubed.

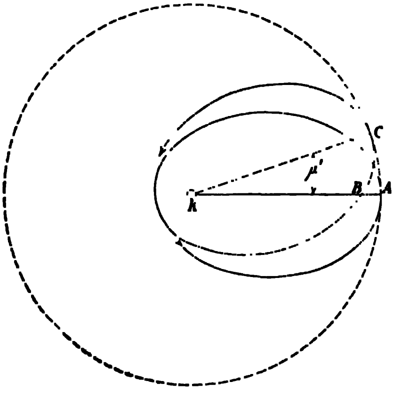

FIG. 73.

As soon as such an (apparent) additional, central force appears, the previously stationary, elliptical orbit begins to rotate as a whole. The "perihelion" is displaced and rotates slowly about the nucleus (see Fig. 73). Thus there is a double motion: the revolution of the electrons in the ellipse (μ) and the motion of the ellipse itself (μ'). The energy U of the total motion can, obviously, be considered as resolved into (1) the orbital energy U_0 of the ellipse considered as stationary, and (2) the energy U' of the perihelial rotation or precession of the ellipse, which is generally small compared to U_0; thus

$$U = U_0 + U'. \tag{279}$$

---

[1] According to Eq (263) the apparent mass of an electron in an elliptical orbit is not constant.

To each of these two rotations belongs a quantum condition, which may be expressed most simply and generally for the kinetic energy, as above (Eq. (273)), by:

$$U_{0k} = \frac{nh\mu_0}{2} \text{ and } U_k' = \frac{n'h\mu'}{2},$$

in which n is the **principal quantum number** and n' **the subordinate quantum number.** Thus for the total energies U_0 and U' we have definite expressions analogous to those of **311.** For U_0 we get as a first approximation the value given by Eq. (277), but a small correction term is involved which introduces the circumstance that even for the electron moving in an ellipse (temporarily considered stationary) it is not *only* the Coulomb force which is effective. For U' the calculation is relatively intricate, inasmuch as μ' depends not only upon n' and the universal constants, but also upon n.

Without going into further details, only the result which is most important for theoretical purposes can be emphasized at this point, namely, that μ', like μ_0 in Eq. (276), cannot assume all, continuously changing values but involves a quantum selection. Since the velocity of precession of the elliptical orbit as a whole is dependent upon the form (eccentricity) of the ellipse, μ' becomes greater as the eccentricity increases. *This, then, is the reason why all ellipses are not possible and why quantum selection is involved.* Expressed in terms of a formula, the result is relatively simple and states: in addition to each circular orbit which is permissible according to the principal quantum conditions, *i.e.*, whose radius essentially satisfies the conditions of Eq. (275), there are a number of possible elliptical orbits whose major axes are equal to the diameter of the circular orbit and whose minor axes satisfy the condition that

$$b = \frac{an'}{n}. \tag{280}$$

Excluding the value $n' = 0$, for which the ellipse degenerates to a straight line and the electron therefore approaches infinitely near to the nucleus, the orbits illustrated in Fig. 74 are obtained by placing whole numbers for n and n' in Eq. (280) up to $n = 4$; the precession of the orbits is, of course, not shown in these diagrams. Furthermore, it is to be concluded from Eq.

(280) that the principal quantum number n is always greater than the subordinate quantum n'; if both were the same, there would be a circle instead of an ellipse. To distinguish the forms and magnitudes of the electron orbits, especially those of the higher atoms, the two quantum numbers offer a very convenient aid. According to Bohr, each individual orbit is represented by $n_{n'}$. We may thus speak of a 4_1 orbit (the largest and longest ellipse in Fig. 74), a 3_3 orbit (the second largest circle in Fig. 74), etc.

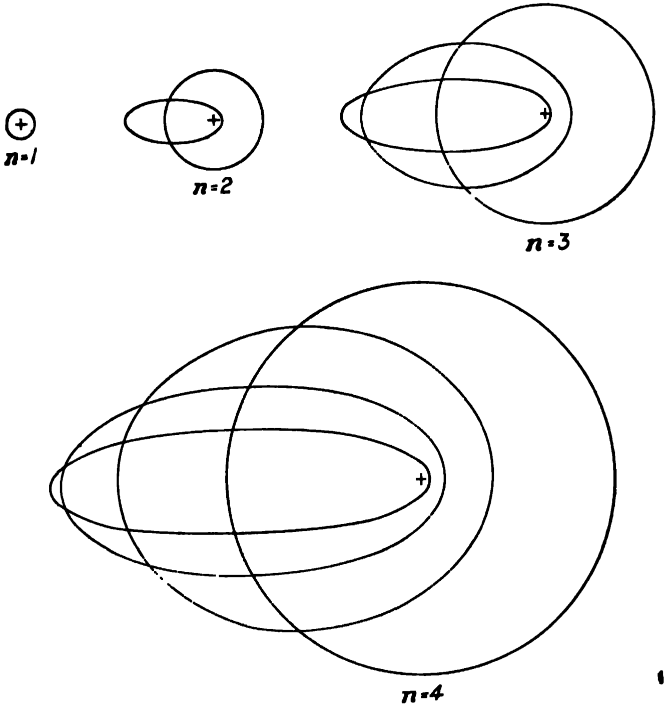

FIG 74

315. The Fine-structure of Spectral Lines Due to Relativity Effect of Velocity on Mass.—If now Eq. (279) is introduced into the frequency law (Eq. (267)), the following is obtained for the frequency of the spectral lines:

$$\nu = \frac{1}{h}(U_{01} - U_{02}) + \frac{1}{h}(U_1' - U_2').$$

Since U' is small compared with U_0 (the same holds for the differences), a spectral line is essentially characterized by a definite jump of the actual orbital energy U_0. However, due to the presence of U', the line does not appear homogeneous, but, because of the discontinuous variation in U', it is resolved into a number of lines lying very close together; in other words, *spectral lines have a* **"fine structure."** By means of Eq. (280) the number of components into which a single spectral line resolves may be determined without difficulty. Each elliptic orbit which is possible according to Eq. (280) corresponds to a definite rotational velocity μ' of the perihelion and therefore to a definite value of U'. For example, in the Balmer line H_α the number of initial orbits is $3(n = 3)$, of final orbits $2(n = 2)$; thus, a total of $3 \times 2 = 6$ closely neighboring lines are to be expected. But since the differences between the U' values of the three initial orbits are smaller than those of the two final orbits, the six components present in this spectral line separate into two somewhat more widely spaced groups each consisting of three lines lying very close together. With hydrogen, due to its singly charged nucleus, the value of U', and therefore the separation of these lines, is very small; on this account the finest apparatus available at present has only succeeded in experimentally resolving the H_α line into the two groups.

The experimentally determined distance between them (about 0.14 Å) agrees very well with the result of the complete theory (first developed by Sommerfeld), so that the fundamental conceptions, especially the assumption that discrete elliptic orbits are present, may be considered as experimentally proved, even though the proof is indirect. Moreover, in the higher atoms, whose nuclear charges are greater than that of hydrogen, the separation of fine-structure lines is considerably greater, at least for the spectral lines sent out by the more deeply situated electrons but here the relationships are less simple than for hydrogen.

316. The Nodal Motion of the Orbital Planes of the Electrons. If another external force acts upon the electron besides the forces which obey Coulomb's law (somewhat modified, if need be) then the whole plane of the orbit begins to rotate or precess in space—the *orbital plane performs what is called a* **nodal motion** *or precession.* To describe this rotating motion a plane XY is established perpendicular to the direction of the external force Z (see Fig. 75); the line of intersection of this plane with the orbital plane, the so-called *"nodal line," then rotates with a certain rotational velocity μ'' about the direction of the external force.* In principle, the considerations in **314** are now repeated: the total energy of the electron in its revolution about the nucleus is composed of three parts—the energy U_0 of the original elliptic orbit (considered stationary), the energy U' of the perihelial motion, and, finally, the energy U'' of the nodal motion. For this new motion again, there is a special quantum number, the so-called **equatorial quantum number** n'', so that the complete quantum representation of the whole motion requires three quantum numbers.

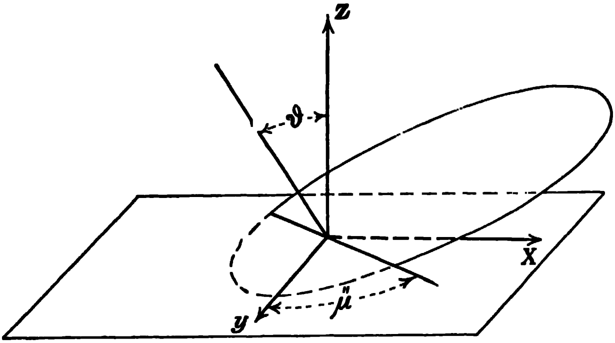

Fig 75.

317. The Zeemann and Stark Effects.—The simplest example of a case where nodal motion of electron orbits within the atom occurs is given by the effect of a magnetic field. In optical experiments this made itself manifest in the discovery by Zeemann (1896) that a spectral line which was approximately sharp in the beginning was resolved into several components. If a beam of light emitted by a gas placed in a magnetic field is observed at right angles to the field, then in the simplest cases the **normal Zeemann effect** is obtained; in addition to the original spectral line which is now polarized parallel to the magnetic field, a new component is found on each side of it which is polarized perpendicular to the field. If the observations are made parallel to the field, only the two new components are present and they are oppositely circularly polarized. The distance between the components in such cases is always proportional to the strength of the magnetic field. It is noteworthy that this effect, as H. A. Lorentz had shown even before its experimental discovery, may be deduced from the classical electromagnetic theory of light, and for a time served as a support for it. However, Sommerfeld (1916) succeeded in proving that it also fitted in remarkably well with the quantum theory.

Of the results of these calculations, only one can be mentioned here: just as in the plane only a certain number of elliptical orbits are possible due to the quantum conditions, so in the nodal motion due to the magnetic field not every slope of the orbital plane with respect to the direction of the force is possible, but only those which satisfy the condition (see Fig. 75) that

$$\cos \vartheta = \frac{n''}{n'}.$$

Thus a directional quantization takes place as soon as a nodal motion is added to the perihelial motion.

It is noteworthy that Gerlach and Stern[1] were able to establish this result experimentally by means of the following investigation. A straight beam of vapor consisting of silver atoms was conducted through a non-homogeneous magnetic field; if all positions of the atoms with respect to the magnetic field were possible, then the original beam must have been somewhat deflected and must have appeared continuously broadened by the magnetic field. Actually, the beam was split into two sharp components which corresponded to the quantum numbers $n'' = n' = 1$ not only qualitatively but quantitatively. (The case of a quantum number $n'' = 0$ is to be excluded as physically impossible on the same grounds as for n'.)

The effect discovered by Stark (1913) consists in the splitting of one sharp spectral line by means of an electric field into a number of components which, when examined transversely (the direction of observation is perpendicular to the electric field), are polarized partly parallel and partly perpendicular to the direction of the field. While according to classical theory an electric field would be expected to have absolutely no effect on spectral lines, or at most a very trifling one, the quantum theory of the Stark effect, developed first by Epstein and Schwarzschild (1916), is in very good agreement with the observations. The electron orbits are considerably more complex in the Stark effect than in the Zeemann effect, even if the relativity effect on the mass is entirely neglected; the minor axis of the elliptic orbit varies back and forth between two limiting values with the same period as the nodal motion.

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[1] *Z. Physik.*, **8**, 110 (1921); **9**, 349 (1922).

318. The Correspondence Principle.[1]—By means of the previously discussed assumptions of the quantum theory it is only possible to calculate the frequency of a spectral line; nothing can be said concerning the other optically observed properties of spectral lines, the intensity, the state of polarization, the ability to show interference phenomena, etc. Closing this gap involves difficulties because a more exact knowledge of the process of emission is required. However, Bohr succeeded in evading this by means of the following considerations: for relatively slow motions (high values of n) the laws of quantum theory, which are still partially unknown, must transform completely into the better known classical laws; therefore, for rapid motion (small quantum numbers) a certain relationship (*correspondence*) between the two must remain. It has already been shown in **311** that for high quantum numbers the frequency ν emitted by a circular orbit was really the same as the rotation frequency μ corresponding to the demands of classical theory. Proceeding towards the smaller quantum numbers, this equality disappears, yet the emitted frequency ν always lies between the rotation frequencies μ_1 and μ_2 of the initial and final orbits. It was then further concluded that quantum jumps, which appear possible according to the frequency law (Eq. (267)), are, in reality, only permissible when extrapolation into the region of higher quantum numbers results in no disagreement with any of the classical laws. For example, it can be seen immediately (**311**) that in circular motion by no means all quantum jumps lead to the equality of ν and μ, but only those jumps for which $\Delta n = 1$. Thus, *in a pure harmonic (sine-wave) motion, such as a circular*

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[1] See also BUCHWALDS, E., "Das Korrespondenzprinzip," Braunschweig (1923); * SOMMERFELD, *loc cit*, p 577; ANDRADE, *loc. cit*, p. 159 *et seq.*, p 217 *et seq*, *cf* also final footnote to this paragraph.

motion represents, only electron jumps into neighboring orbits are possible.

The relations are different for electron orbits other than circular, *e.g.*, for the elliptical Kepler orbits. The motion in such an elliptical orbit can be considered as being composed of a number of harmonic motions just as an ordinary musical tone can be resolved into a number of "pure tones," the "fundamental" and the "overtones";[1] thus, if an electron from such an orbit radiates electromagnetic waves according to classical theory, then there are found existing simultaneously in the waves the fundamental vibration μ and its overtones (2μ, 3μ, .). Of course, the quantum theory has nothing in analogy with a simultaneous emission of a fundamental and several overtones by a simple vibrating system, yet *it can at least explain the emission of individual overtones simply by means of a single quantum jump of several units;* for example, by repeating the process of reasoning in **311** for large quantum numbers the first overtone ($\nu = 2\mu$) is obtained by means of the quantum jump $\Delta n = 2$, the second overtone ($\nu = 3\mu$) from $\Delta n = 3$, etc. *Each overtone vibration of the stationary orbits thus corresponds to a definite quantum jump; e g.*, if in two stationary orbits the overtone vibration with the frequency 5μ is lacking, then, according to the correspondence principle, a quantum jump of five units is impossible; since the overtone concerned cannot be present according to classical theory, its emission must likewise be impossible on quantum theory. However, these considerations hold not only for the jumps of the principal quantum number n but also for those of the subordinate quantum number n'. Now since the perihelial rotation μ' always represents a pure harmonic (circular) motion (therefore overtones can never occur), the subordinate number corresponding to μ' can change by only one (± 1) unit.[2] From this it follows that the electron cannot perform jumps between any optional elliptical or other orbits, even when the overtone vibrations corresponding to the quantum jumps are present, but only between orbits whose subordinate quantum numbers differ by just one unit.[1]

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[1] See BUCHWALDS, *loc. cit*, p 48, concerning the resolution of an elliptical Kepler motion into harmonic components

[2] This selection principle of the subordinate quantum number has been derived in a totally different way by Rubinowitz (*Physik. Zeit*, **19**, 441 (1918)). However, according to Rubinowitz, the quantum jump 0 must also be permissible, which does not appear to agree with experience.

In a similar manner a selection principle may be derived from the correspondence principle for the equatorial quantum number n'' also; in this case, of course, it is permitted to have jumps of $\Delta n'' = 0$ as well as $\Delta n'' = \pm 1$.

On the basis of the correspondence between the presence of certain overtone vibrations in the stable electron orbit and the occurrence of definite quantum jumps, it is not only possible to decide whether a given spectral line will occur or not, but it is also possible to estimate its relative intensity. The more strongly pronounced the overtone vibration corresponding to the quantum jump the more frequently will that quantum jump occur and therefore the greater will be the intensity of the spectral line. This sort of calculation was employed by Kramers for the theoretical determination of the relative intensities of the components of several spectral lines resolved by means of the Stark effect as well as the relativity change of mass with velocity; this led to a satisfactory representation of observations which at first seemed quite irregular.

As Bohr himself always emphasizes, the correspondence principle has a purely formal character at the present time, yet without doubt it is suitable for indicating the way which leads to clearing up some of the details involved in the actual process of the emission of spectral lines, concerning which we are still working in the dark. It appears as if the correspondence principle, which is based upon classical theory, supports the characteristics of the intermediate orbit calculation, for these the classical radiation laws hold to some degree of approximation: between two orbits with the fundamental frequencies μ_1 and μ_2, an intermediate orbit apparently can exist only when two corresponding harmonic overtone vibrations $n\mu_1$ and $n\mu_2$ are present in the stationary orbits. The more pronounced these overtone vibrations the greater is the probability that the electron actually enters the intermediate orbit and thus emits a frequency of approximately $\frac{n}{2}(\mu_1 + \mu_2)$.[1]

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[1] Under *special* experimental conditions this selection principle frequently breaks down; *e.g.*, J. Stark (*Ann. Physik*, **56**, 584 (1918)) has observed series in helium in *a strong electric field* in which the subordinate quantum number changed either two units or not at all.

[*] However, a more detailed examination of the correspondence principle indicates that this is precisely what would be expected; in fact, Bohr predicted that it should happen before Stark's work was published. See Part II of "The Quantum Theory of Line Spectra" (in English), Danish Academy of Science (1918), p. 69, especially the footnote. These two papers by Bohr and the one by H. A. Kramers on "The Intensities of the Spectral Lines," also published in English by the Danish Academy (1919), form a most important part of the literature on quantum theory.

γ Spectra Similar to the Hydrogen Spectrum

319. The Fowler and the Pickering Series.—In spectral (discharge) tubes containing a mixture of hydrogen and helium, Fowler observed a series which could be expressed by the formula

$$\nu' = \Re\left(\frac{1}{1\ 5^2} - \frac{1}{m^2}\right)(m = 2, 3, 4\ .\qquad) \qquad (281)$$

and which was first ascribed to hydrogen.

In the spectra of nebular stars Pickering discovered the series

$$\nu' = \Re\left(\frac{1}{2^2} - \frac{1}{\left(m + \frac{1}{2}\right)^2}\right)(m = 2, 3, 4\qquad), \qquad (282)$$

which later was also produced in spectral tubes.

Disregarding for the moment the possible differences between the Rydberg constants of different elements (**312**),[2] the Pickering series will have the same limit as the Balmer series for hydrogen (as Eq. (282) indicates) and its lines will always fall in between the lines of the Balmer series. For example, if it was permissible to use values of m which were not whole numbers, *e.g.*, values such as $2\frac{1}{2}$, $3\frac{1}{2}$, etc., then the Balmer series would be obtained directly. The origin of the Pickering series was therefore supposed to be the hydrogen atom.

This supposition was supported by the discovery that there were also lines with $m = 2\frac{1}{2}$, $3\frac{1}{2}$, etc., which really belonged to the Pickering series but which appeared to coincide with the

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[1] * See however the footnote to **296.**

[2] The observations upon which Eqs. (281) and (282) were based were not at first of sufficient accuracy to permit anything certain to be said regarding the magnitude of Rydberg's constant

Balmer lines and thus remained hidden for a long time. In order to avoid current numbers m which are not whole numbers, it is expedient to write Eq. (282) in the form

$$\nu' = 4\mathfrak{R}\left(\frac{1}{4^2} - \frac{1}{m^2}\right) \ (m = 5, 6, 7 \qquad). \tag{282a}$$

In the same way, the Fowler series can be written

$$\nu' = 4\mathfrak{R}\left(\frac{1}{3^2} - \frac{1}{m^2}\right) \ (m = 4, 5, 6\ . \qquad). \tag{281a}$$

Thus the Fowler series corresponds completely to the Paschen series except for the factor 4.

A more exact examination now showed that the *Rydberg constant in Eqs.* (281*a*) *and* (282*a*) *corresponded to helium and not to hydrogen.* The conclusion that both these series were due to helium was experimentally confirmed by Stark, who succeeded in detecting under certain conditions (in the presence of a strong electric field) both the Fowler and the Pickering series in spectral tubes filled with pure helium.

320. The Influence of Increased Nuclear Charge.—It may be shown that *the factor* 4, which is the main difference between the hydrogen spectra and the spectra Eq. (281*a*) and (282*a*), *is due simply to the double charge on the helium nucleus.* Repeating the process of reasoning which led to the expression (Eq. (278)) for Rydberg's constant, but with a nucleus of Z charges instead of a unit charge, it is first found that

$$U_k = \frac{m}{2}a^2\omega^2 = \frac{1}{2}\frac{(Ze_0)e_0}{a} = \frac{nh\omega}{4\pi}.$$

From this it follows that the expression for a (Eq. (275)) must be multiplied by $\frac{1}{Z}$, while the value of the Rydberg constant represented by Eqs. (278) or (278*a*) must be multiplied by Z^2. Thus the following equation is obtained for the spectrum:

$$\nu' = \mathfrak{R}Z^2\left(\frac{1}{n^2} - \frac{1}{m^2}\right). \tag{283}$$

For a doubly charged nucleus such as must be assigned to the helium atom because it is the second atom in the periodic system of the elements, the factor becomes $4\mathfrak{R}_{He}$. The present simple calculations hold merely for the case in which a single electron revolves about the nucleus. *The origin of the Fowler and Picker-*

ing series is therefore not to be sought in the neutral helium atom but in the singly charged (positive) ionized helium atom ($Z = 2$; *1 electron*).

While the spectra of the neutral helium atom, which has two electrons revolving about the nucleus, cannot be represented by an equation of the form of Eq (283), it must be possible to do so in the case of a doubly charged lithium atom which consists of a nucleus with three charges and a single electron. The spectra of this must be of the form $\nu' = 9\mathfrak{R}_{Li}\left(\frac{1}{n_2} - \frac{1}{m_2}\right)$; indications of its existence indeed appear in the spectra of certain nebular stars, yet a positive proof of this form of equation has not been found up to the present time.

δ The Spectra of the Higher Atoms

321. General.—An atom consisting of a nucleus with more than one charge and the corresponding number of electrons is able to emit a very much greater number of spectra than a hydrogen atom; a part of these spectra originate in energy transitions of electrons revolving "inside," close to the nucleus (the **internal spectra**), another part from energy transitions of the outer electrons (the **external spectra**). Although no sharp boundary is to be drawn between these two kinds of spectra, they are generally quite noticeably different from each other. While the first kind lie in the extremely short wave lengths, mostly in the X-ray region, due to the nearly complete effectiveness of the total nuclear charge Z (*cf.* Eq. (283)), a single outer electron is affected by a force of the order of magnitude of a *single* elementary charge, since the remaining ($Z - 1$) electrons act in opposition to the Z-charges on the nucleus.[1] Therefore, the orbital energy of these outer electrons is of the same order of magnitude as in hydrogen, so that the spectra depending upon them *lie in the ultra-violet or visible portion of the spectrum;* in this they are again similar to hydrogen.

Compared to the H atom and the He ion, an exact calculation of the spectra of the higher atoms has not yet been performed successfully because the consideration of the mutual effects between the outer electrons involves great difficulties. Here, again, there is a problem such as frequently occurs in astronomy, *e g.*, in the calculation of the disturbing effect produced by other

[1] * This is the so-called **screening effect** of the electrons.

planets on a given orbit, but the mutual effects among actual planets are considerably less than among the electrons of an atom. Thus, on account of the complexity of the calculations, investigators must resort to the use of simplifying assumptions and approximation methods; for this reason alone it must be expected that the results will be much less exact than for the hydrogen atom.

An approximate calculation of the orbital energy U of an electron in a complex atom can be performed by means of an expression which is directly related to Eq. (283):

$$U = \Re h\nu_l \frac{Z^2}{n^2},$$

in which the true nuclear charge number Z must be replaced by an **"effective" nuclear charge** Z^*, and the true quantum number n by an **"effective" quantum number** n^*; this gives

$$U = \Re h\nu_l \frac{Z^{*2}}{n^{*2}}.$$

The apparent change in the nuclear charge is due entirely to the **screening effect** of the other electrons on the nuclear charge; therefore Z^* is always smaller than Z. The apparent change in the quantum number is due to the same cause. In the simpler cases, such as the X-ray spectra, it is sufficient to change Z to Z^* and retain the value of n; more complex cases, such as when Z^* changes during the period of revolution of the electron, are easier to treat if n^* is introduced into the calculation.

In certain individual cases it was possible to perform an exact calculation; Kramers[1] with the assistance of a special method was able to calculate rigorously the work of ionization of neutral helium. He assumed that the previously accepted laws, which were satisfactorily confirmed for hydrogen, were correct. No agreement could be obtained between theory and the observed results. If the assumed model of the helium atom is correct (see **330**), as it very probably is, one of the more general assumptions upon which the calculation was based must be unsuitable. Since the theoretical difference between the higher atoms and the hydrogen atom is that the individual (emission) electron is affected not only by a static electric force on the part of the nucleus but also by a varying force due to the motion of the neighboring electrons, *the present disagreement probably arises because in rapidly changing fields the laws previously applied require fundamental change or extension.*

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[1] *Z. Physik.*, **13**, 312 (1923).

322. The Measurement of the Wave Length of the X-rays by the Reflection Method.—Before proceeding to the closer examination of the X-ray spectra which are sent out from the electrons situated close to the nucleus, and their laws, the most important methods for the exact measurement of these wave lengths will be briefly described.[1] The basis upon which all methods for the measurement of such wave lengths are founded is the discovery (Laue, 1912) that the regular arrangement of the atoms in crystals represents a three-dimensional diffraction grating for the X-rays.[2] For practical purposes Laue's original method, in which the diffraction of a ray passing through a crystal was measured, is less applicable than the one developed by W. H. Bragg (the "reflection-angle" method), in which the X-ray beam is considered as being simply reflected from a crystal plane. The latter method depends upon the following phenomena:

Only a small fraction of a beam of X-rays with a definite wave length λ striking upon a crystal surface will be reflected from the real surface; the main portion penetrates into the interior. The same, relatively small, fraction of the beam will be reflected at every layer of atoms (**lattice plane**). Since the reflection from any single atomic plane is very weak, the intensity of the reflected rays becomes perceptible only when the waves coming from the different parallel planes reinforce each other by interference phenomena. In order that this should occur, the paths of the waves reflected from a single plane must differ either by exactly one wave length or by a whole number (n) times the wave length. The condition for this is expressed (see Fig. 76) by:

$$n\lambda = CD + DB - AB = DB - DE = DF - DE = EF = 2d \sin \alpha, \tag{284}$$

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[1] An excellent discussion of these methods is given by P. P. Ewald, "Kristalle und Rontgenstrahlen," Berlin (1923); also Bragg, W. L. and W. H., "X-rays and Crystal Structure," London (1924); Siegbahn, *Jahr. Radioakt. Elektronik*, **13**, 296 (1916); *Siegbahn, "Spektroskopie der Rontgenstrahlen," Springer, Berlin (1924)

[2] For a general summary see Laue, M. v, *Jahr. Radioakt. Elektronik*, **11**, 308 (1914).

where d denotes the distance between neighboring parallel atomic planes. When λ (monochromatic light) and d are both fixed, it is evident that only α is variable, or if the angle of incidence is varied, a perceptible reflection will occur only at certain definite values α_1, α_2, . . . , which are called the *reflection angles* of the particular wave length used.

In order to measure an X-ray spectrum (generally excited by bombarding a metallic surface with cathode rays), the crystal is turned slowly about one of its axes so that it passes through all angles and the angles at which the reflected X-rays have especially high intensity are determined. In order to obtain λ in absolute units, the distance between the atomic planes must be known as accurately as possible. In the simplest cases, if the atoms are arranged with complete symmetry in cubes and the mean distance Δ_0 between the atoms is simply equal to the distance d between the layers, this length Δ_0 follows directly from Eq. (255), for the solution of which an accurate knowledge of Avogadro's number **N** and the atomic volume is required.

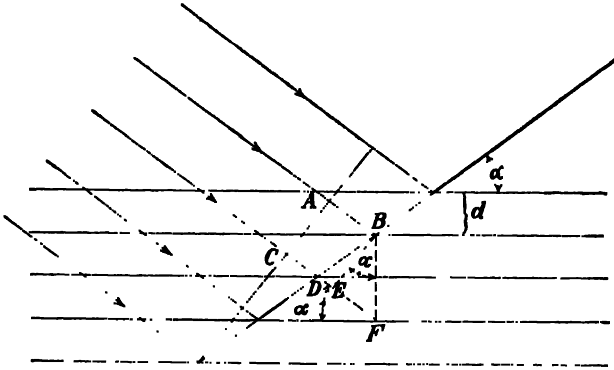

Fig. 76

An example showing how sharply the X-ray spectrum can be photographed at the present time is given in Fig. 77, page 502, which shows a portion of the X-ray spectrum of ytterbium.

323. The K-, L-, M-, and N-series.—The results which have been obtained up to the present on the X-ray spectra of atoms may be summarized as follows: each element emits several series of spectra; the structures of the spectra of the elements are all quite similar. With respect to wave lengths, the various series for a single element are widely different, so that, contrary to the majority of spectra (of the hydrogen type) lying in the visible region, they cannot be brought into coincidence. The series with the shortest wave lengths is called the K-series. It consists of only three plainly distinguishable groups of lines (K_α, K_β, K_γ) which, in general, can be further resolved into a number of single lines, e.g., up to the present a maximum of seven α-lines has been found: K_{α_1}, K_{α_2}, K_{α_3}, etc.

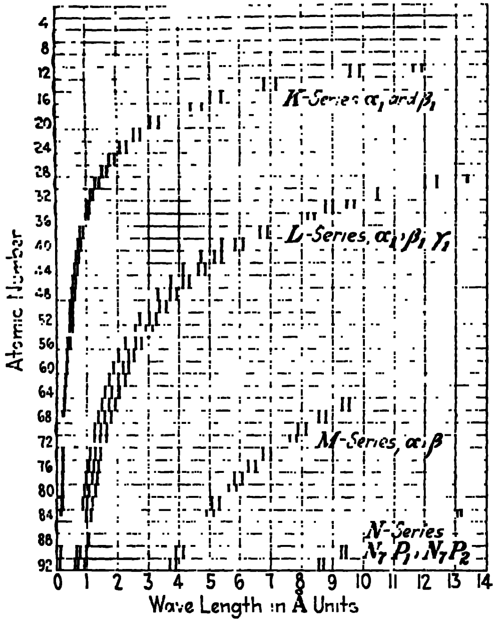

Fig 78

The next series, which has longer waves, is the L-series; in it fourteen lines could be found, but, of course, not in all elements.

After this comes the M-series, which has a relatively complex structure and probably consists of a larger number of lines than has yet been measured.

Finally, there is the N-series, of which only a few members have been found, and these only in the heaviest elements.

Figure 78 gives a survey of the change in the series from element to element; the X-ray spectra of the elements are simply plotted under each other in the order of the atomic numbers.

It will be seen that, with increasing atomic number, the spectra are displaced in an absolutely regular manner from longer to shorter wave lengths. Since the shortest wave length which has yet been measured with certainty is about 0.15 Å., the longest about 13 Å., it has only been possible to measure the L-, M-, and N-series for the elements of high atomic weight; for those of lower atomic weight only the K-series has been measured, and these merely down as far as sodium.

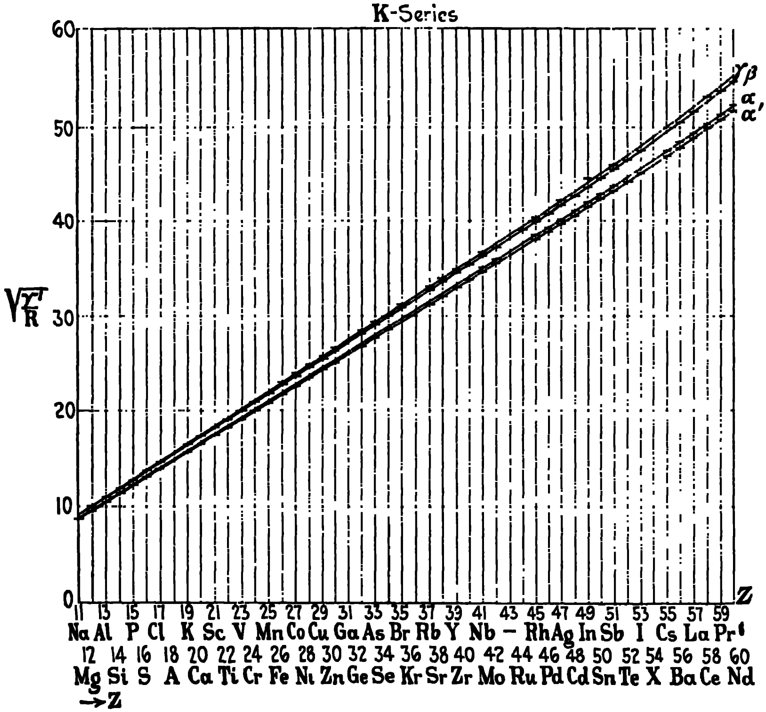

FIG 79.

This behavior of the X-ray spectra is, as has already been emphasized in **263**, in complete antithesis to the optical spectra which have a decided periodicity.

As Moseley (1913)[1] showed, the regularity in the displacement of the K-series lines from element to element is most clearly indicated when the quantity $\sqrt{\nu'}$ or $\sqrt{\frac{\nu'}{\mathfrak{R}}}$ is plotted as a function of the atomic number. The resulting graph for each spectral line K_α, K_β, K_γ is very nearly a straight line (see Fig. 79).

According to Moseley, the displacement of the K-line may be expressed mathematically by

$$\sqrt{\frac{\nu'}{\mathfrak{R}}} = 0.866(Z - 1) \simeq \sqrt{\frac{3}{4}}(Z - 1)$$

or

$$\nu' = \mathfrak{R}(Z - 1)^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right), \tag{285}$$

an equation which hints at a close relation between the K-spectrum of the higher atoms and the Lyman series for hydrogen. The first line of the L-series, for the elements investigated up to the present, may be represented by the equation

$$\nu' = \mathfrak{R}(Z - 7.4)^2\left(\frac{1}{2^2} - \frac{1}{3^2}\right), \tag{285a}$$

which may be compared with the Balmer series.

324. Conclusions Regarding Atomic Structure Drawn from the Internal Spectra.[2]—Although Eqs. (285) and (285*a*) do not give a quite exact representation of the facts, yet it follows with absolute certainty that the fundamental orbit of the K-series is a one-quantum orbit ($n = 1$) and that of the L-series a two-quantum orbit ($n = 2$). For the higher X-ray series no simple formula, not even an approximately valid one like Eqs. (285) or (285*a*), can be given, but, by considering the phenomena of these series as a whole, the following general conclusions can be drawn:

The existence of individual, widely separated spectral series leads directly to the fundamental conception that a number of electron groups are present in the atom which differ considerably from each other with respect to orbital energy and the distance between the electrons and the nucleus. *Therefore, a single series*

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[1] * *Phil Mag*, **26**, 1024 (1913); **27**, 703 (1914)

[2] See particularly the article by Bohr and Coster, *Z. Physik*, **12**, 342 (1923).

arises from the transition of an electron from one of the outer groups (*e.g.*, the L-, M-, or N-groups) *to one of the inner groups* (*e.g.*, the K-group). The fine structure of the individual lines is due to the energy differences within a definite group; for example, the $K_{\alpha 1}$ and $K_{\alpha 2}$ lines are to be explained by transitions from

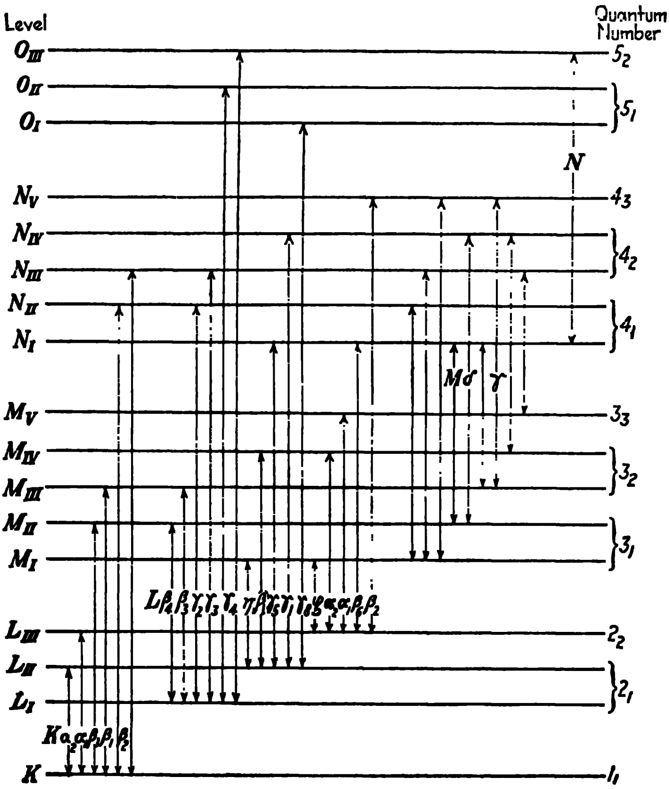

Fig 80

two somewhat different L-orbits to a single K-orbit (according to Wentzel the remaining K_α-lines probably do not occur under normal circumstances, but only in ionized atoms of more than one charge).

Just as in the above for the H atom, a number of energy levels may be ascertained from the various spectra, for, according to the frequency law, each spectral line corresponds to the difference between two energy levels. The result of such investigations for elements whose atomic numbers are in the neighborhood of 54 are represented diagrammatically by Fig. 80,[1] from which the number of the levels known at the present time and the spectral lines arising from individual transitions may be seen [2]

It was first attempted to explain the difference between the levels of a single group, which has a definite principle quantum number, by differences in the subordinate quantum number (the orbits are thus partly circular, partly elliptical), but the number of levels is actually greater than the number of values possible for n'. Formally, this condition is accounted for by introducing one more quantum number, the exact physical significance of which has not yet been interpreted.

A graphic representation, from which the absolute values of the individual energy levels of all elements can be taken, is given in Fig. 81, in which $\sqrt{\frac{U}{\Re \mathrm{V}_l h}} = \frac{Z^*}{n}$ (see **321**) is plotted as a function of the atomic number Z. As a matter of principle all the X-ray lines of the individual elements in the normal ionized state can be found from these curves. For example, the wave number ν' of the L_{β_3}-line of Ag ($Z = 47$) corresponding to a transition from the $\mathrm{M}_{\mathrm{III}}$-level to the L_{I}-level is found to be $\nu' = \Re(16\ 7^2 - 6.42^2) = \Re \times 238 = 109737 \times 238 = 2.61 \cdot 10^7$ *cm.*$^{-1}$, *i.e.*, the wave length $\lambda = 3\ 83$ Å.

Now, putting $n = 1$ for the K-group, $n = 2$ for the L-group, etc., the effective nuclear charge Z^* can obviously be determined from the behavior of curves of $\frac{Z^*}{n} = f(Z)$ in Fig. 81. Even without a special calculation we can see that Z^* in the different levels, especially for the heavier atoms, does not vary in the same way with increasing Z. According to Bohr, important conclusions regarding the structure of atoms can be drawn from this behavior.

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[1] The distances between the individual groups are drawn relatively too small, those between members of the same group too large

[2] The presence of the line in the N-series as well as several of the lines in the M- and L-series have not yet been directly observed in the elements in question, but have been assumed in analogy with the heavier atoms.

The difference between the true nuclear charge Z and the effective nuclear charge Z^*, the so-called "Kernladungsdefekt,"[1] is due, as has already been indicated, to the effect of all the elec-

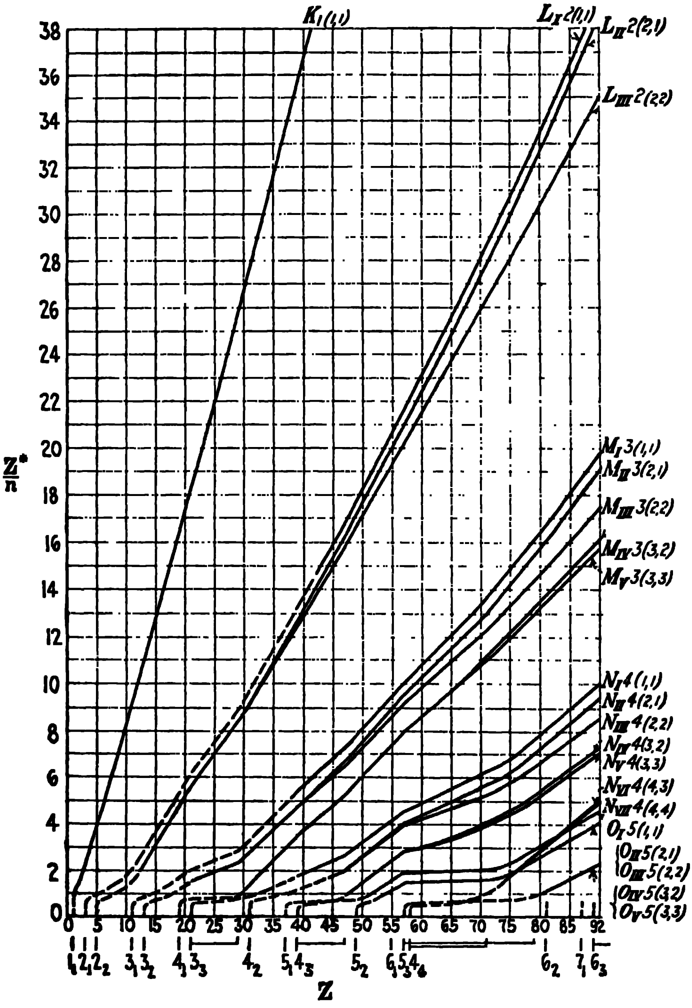

Fig 81

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[1]* This "*nuclear-charge defect*" is frequently called the *screen number* or *screening constant* and is designated by s; thus $s = Z - Z.^*$ (See SOMMERFELD, *loc. cit.*, p. 498.)

trons of the outer portion of the atom. For example, if it is assumed that the emitting electron belongs to one of the middle groups, the addition of an electron located *outside* this group has an almost imperceptible effect,[1] while the charge of the electrons located in a deeper layer becomes very much involved in the phenomena as the nuclear-charge defect of Z. Now considering the higher atoms of the series which are formed by increasing the nuclear charge step by step and correspondingly allowing an electron to be added to the atom from the outside, then it is possible to see directly *from the behavior of the nuclear-charge defect or the effective nuclear charge number Z^* whether the new electron stays in the outer portion of the atom or whether its orbit lies entirely or partially in the inner portion.* A steeper slope of the $\frac{Z^*}{n}$-curve, which corresponds to a rapid change of Z^*, *i.e.*, a slight change in the nuclear-charge defect, indicates that, in comparison with the group containing the emitting electron, the newly added electron lies relatively far out in the atom; a smaller slope indicates a perceptible increase in the nuclear-charge defect and thus that the new electron approaches somewhere near the group concerned. If a portion of the curve is quite horizontal, it means that the increase of true nuclear charge is the same as the increase of the nuclear-charge defect, *i.e.*, the new electron enters into a group which is closer to the nucleus than the emitting electron.

In view of these considerations, the following conclusions regarding atomic structures may be drawn from the breaks in the $\frac{Z^*}{n}$-curves of Fig. 81. In the elements 21 to 28 the entering electron for the first time takes up a position which is not in the outer but in a deeper portion of the atom. This is repeated with the elements 39 to 46. The most striking cases are found in the elements from 58 to about 72, in which the new electron appears to penetrate particularly deep into the atom. From the magnitude of the changes of slope it can be concluded that in the first two cases the new electron takes up a position in the M- or N-groups; but in the last case also the electron must fall into the N-group, since in the O-group, which is still farther from the nucleus, the increase of nuclear charge is entirely compensated by the nuclear charge defect.

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[1] In this case the relations are similar to those of electrostatic processes within a metallic, conducting, hollow sphere which are known to be independent of the charge on the sphere itself.

Since the quantity $\frac{Z^*}{n} = \sqrt{\frac{U}{\Re \nu_l h}}$ represents a direct measure of the orbital energy (work of removal to infinity), Fig. 81 further indicates the remarkable result that up to about $Z \simeq 75$ it is easier, but above that more difficult, to remove an electron of the subgroup N_{VII} from the atom than from O_I or O_{II}. From the absolute values of the nuclear-charge defects of the individual levels, it must be theoretically possible to determine the number of electrons in each group for the different elements. However, apart from the theoretical difficulties mentioned at the end of **321**, this calculation cannot easily be performed in an exact manner; for example, it must be considered that the removal of an electron from an inner group simultaneously involves a change in the effective nuclear charge and thus a change in the energy of all the outer groups The gap in our knowledge occasioned by this fact may, fortunately, be bridged by relatively simple considerations which involve the periodic character of the chemical properties of elements and which give directly the number of electrons in each group (see **347**).

325. Excitation Conditions for the Internal Spectra.—With regard to the conditions for exciting the internal spectra, it must be noted that there is an important distinction in comparison with the external spectra, due to the fact that, as a rule, all inner groups (K-, L-, M-groups, etc) already contain their maximum numbers of electrons and this number cannot be exceeded; stated otherwise: the inner groups are completely "filled," while some of the orbits in the outer portion of the atom are generally free; to these the electrons of the surface of the atom will be "raised" and from them they will return to the normal state accompanied by the emission of an optical wave.

The emission of an X-ray line thus can occur only if an inner electron is first removed entirely out of the atom or at least to one of the unoccupied orbits of the outer portion. For example, the emission of the K_α-line can take place only if an electron of the K-group is first entirely removed from the atom, so that in this group place for one electron is left free. If an electron from the L-group falls into it, a K_α-line is emitted, or if the electron falls from the M-group, a K_β-line results. The place left open in the L- or M-group is, then, soon after occupied by an electron from a still more distant group, etc. The electrons thus fall back into the K-ring by a process which, to a certain degree, takes place as a series of steps, but jumping over several steps, and even the direct return of an outer electron to the K-ring is not unusual.

The energy for raising an electron from the inner portion to the surface of the atom can be absorbed either from rapidly moving electrons (cathode rays) or primary X-rays. In the first case the energy of the impinging electrons must be at least $E_0 e_0 = h\nu_l$, where ν_l is the limiting frequency of the K-series and E_0 the potential across the tube.

As Webster has shown by experiment, when the potential through an X-ray tube is gradually increased, the series of lines K_α, K_β, K_γ do not appear in order (as was the case in the experiments described in **318**), but the whole spectrum appears at one time as soon as the potential $E_0 = \frac{h\nu_l}{e_0}$ is exceeded, at which the energy is sufficient to remove an electron completely from the atom.

If the substance to be excited is illuminated with primary X-rays, the beginning of the excitation may be recognized by the consumption of energy, *i.e.*, by an absorption of the radiation falling upon the substance. In agreement with the conception that an electron of the K-group cannot be raised directly into the L- or M-groups, experiment shows that the K-lines, just like lines of the other spectra, do not appear in absorption; an absorption first takes place when the frequency of the radiation applied exceeds the limiting frequency ν_l of the particular series concerned. Since above the limit every wave can be used for excitation, on the other side of the limiting frequency ν_l a continuous absorption spectrum for each series is obtained. Of course, the beginning of the absorption spectrum is not quite sharp, but has several, very closely neighboring absorption lines which correspond to the above-mentioned transitions of the electrons into the unoccupied orbits located in the outer portion of the atom.[1]

326. The External Spectra of the Higher Elements. General. The external spectra of the higher elements may be resolved into the arc spectrum and the first and second spark spectra. The production of these spectra depends, as their names indicate, upon the conditions under which they are excited, and therefore they generally do not appear simultaneously. We may state with certainty that *the arc spectrum is due to the neutral atom, the first spark spectrum to the ionized atom with a single (positive) charge, and the second spark spectrum to the ionized atom with two charges.*

Up to the present it has not been possible to arrange completely all the lines of the external spectra of the higher elements into series, as with hydrogen. First considering the arc spectrum, the relations are simplest for the elements of the first vertical series of the periodic table, especially for the alkali metals. Proceeding further towards the right side of the table, the structures of the spectra as a whole become more and more complex. For the elements of the second and third columns, as well as helium and neon, it is still possible to arrange most of the lines in series; for the remaining elements, the number of lines is so very large that at the most only single series can be sorted out.

For all of the known spectral series of the higher atoms there are several fairly general regularities in behavior; these will be met in their simplest form in the arc spectra of the alkali metals and will be briefly explained in that connection. As far as the spectra of the other elements may be differentiated from them, a greater multiplicity of lines is the chief difference for example, the typical series of the alkali metals resolve into several subgroups for a number of the other elements; in place of the doublets of alkali series, triplets are found, etc.

327. The Arc Spectrum of the Alkali Metals.—The arc spectrum of the alkali metals when produced under normal conditions of excitation, such as in a Bunsen flame, consists of four different series. Figure 82 represents these series for potassium.

The series ending in the shortest wave length is called the **principal series**; the next two are called the **diffuse and the**

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[1] See KOSSEL, W., *Z. Physik.*, **1**, 119 (1920).

sharp series from the appearance of their lines; the last is the Bergmann or "fundamental" series.[1]

The analogy to the corresponding series in hydrogen, the Lyman, Balmer, and Paschen series, is unmistakable.

The appearance of the individual series, neglecting the occurrence of the doublets,[2] is similar to the Balmer series (Fig. 71). In all cases the lines become closer and closer together as the wave length decreases, and the series ceases abruptly at a certain point, the head of the series.

From the figure the following typical regularities are noted:

1. The heads of the diffuse and the sharp series coincide.

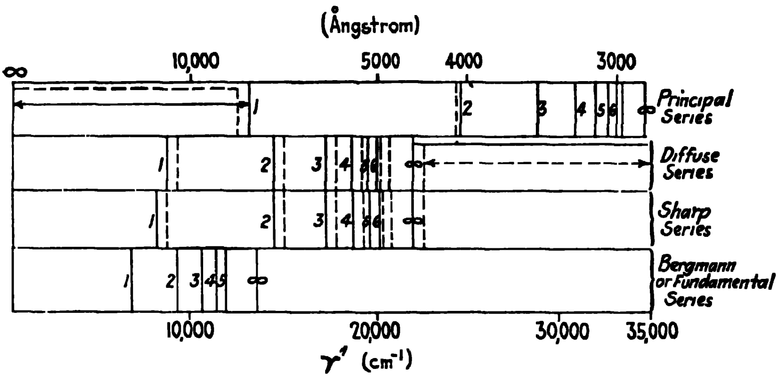

FIG. 82

2. These two series consist of doublets whose components are separated by a constant distance; the head of the series likewise is a doublet which has the same difference of frequency number as the other lines of the series.

3. The principal series also consists of doublets, but the distance between the component decreases as the head of the series is approached, so that the head appears as a single line.

4. The frequency difference between the common head of the diffuse and the sharp series and the head of the principal series

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[1] * Since there is nothing particularly fundamental in the "fundamental series," the term "Bergmann series" will be used to avoid misunderstanding on this point.

[2] In the figure the distances between the two components of the doublets are represented about ten times greater than they would be if drawn to the same scale as the main distances.

is equal to the frequency number of the first member of the principal series (Rydberg-Schuster rule).

The significance of these rules, which remained mysterious for a long time, follows directly from the fundamental conception of the origin of spectral lines, which, in turn, is based upon the frequency law (*cf.* Fig. 72):

1 and 2. Both the diffuse and the sharp series arise from electron transitions from different initial orbits to two similar final orbits.

3. In the principal series the final (normal) orbit is single, the original orbits are double; however, the mutual difference between the two initial orbits diminishes as the size of the orbit increases.

4. The first doublet of the principal series arises from electron transitions from the two final orbits of the diffuse and sharp series to the normal orbit of the principal series.

The representation of the alkali metal series by means of equations may thus be completely fitted into the general form $\nu = \frac{U_1}{h} - \frac{U_2}{h}$. For the individual terms $\frac{U}{h}$ the simpler Balmer expression no longer holds; a more complex function must be introduced. According to Rydberg we can put as a first approximation

$$\frac{U}{h} = \frac{\Re \mathrm{V}_l}{(m + a)^2}, \tag{286}$$

in which a is constant within each series but, in general, is variable from series to series.

Ritz gave the more accurate formula

$$\frac{U}{h} = \frac{\Re \mathrm{V}_l}{[m + a + \alpha f(m, a)]^2}, \tag{286a}$$

in which α is a new parameter, $f(m, a)$ is a function of m and a, which vanishes for large values of m. If we confine ourselves to the Rydberg expression, which, of course, does not represent the spectra of the higher atoms nearly so accurately as the Balmer formula does for the visible hydrogen spectrum, we obtain, for example, for potassium:

Principal series

$$\nu' = \Re \left\{ \frac{1}{(1 + 0.7701)^2} - \frac{1}{\left(m + \begin{Bmatrix} 0.2348 \\ 0.2318 \end{Bmatrix}\right)^2} \right\} (m = 2, 3, 4 \ . \ . \ .)$$

Diffuse series

$$\nu' = \Re\left\{\frac{1}{\left(2+\begin{Bmatrix}0.2348\\0.2318\end{Bmatrix}\right)^2} - \frac{1}{(m-0.1465)^2}\right\}(m = 3, 4, 5. \quad . \;.)$$

Sharp series

$$\nu' = \Re\left\{\frac{1}{\left(2+\begin{Bmatrix}0.2348\\0.2318\end{Bmatrix}\right)^2} - \frac{1}{(m+0.7701)^2}\right\}(m = 2, 3, 4 \;.\;.\;.)$$

Bergmann series

$$\nu' = \Re\left\{\frac{1}{(3-0.1465)^2} - \frac{1}{(m-0.01)^2}\right\}(m = 4,\, 5,\, 6 \qquad .),$$

in which two values of a indicate a doublet.

Written in a more general fashion, the various series are usually designated as the difference of two terms, as follows:

$$\text{Principal series} \quad \left\{\begin{array}{l}\nu_1' = (1,\, s) - (m,\, p_1)\\ \nu_2' = (1,\, s) - (m,\, p_2)\end{array}\right\} \quad m = 2,\, 3,\, 4 \;.\;.\;.$$

$$\text{Diffuse series} \quad \left\{\begin{array}{l}\nu_1' = (2,\, p_1) - (m,\, d)\\ \nu_2' = (2,\, p_2) - (m,\, d)\end{array}\right\} \quad m = 3,\, 4,\, 5 \;.\;.\;.$$

$$\text{Sharp series} \quad \left\{\begin{array}{l}\nu_1' = (2,\, p_1) - (m,\, s)\\ \nu_2' = (2,\, p_2) - (m,\, s)\end{array}\right\} \quad m = 2,\, 3,\, 4$$

$$\text{Bergmann series} \quad \nu' = (3,\, d) - (m,\, f) \quad m = 4,\, 5,\, 6 \;.\;.\;.$$

Thus, there are a total of four kinds of terms, the s-, p-, d-, and f-terms; the constant first terms, or limiting terms, obviously correspond to the negative energy values of the final orbits; the variable second terms, the current or secondary terms, correspond to the energy values of the initial orbits. For example, for the energy of the final orbit of the principal series, which lies deepest in the atom and therefore represents the normal orbit of the outer electron, we have $-U = h\,\mathrm{V}_l\,(1, s)$; in the special case of the potassium atom we have,

$$-U = \frac{\Re h \mathrm{V}_l}{1.7702^2} = \frac{109737 \times 6.54 \times 10^{-27} \times 3 \times 10^{10}}{1.7702^2} = 6\,87 \cdot 10^{-12}\ \textit{erg}.$$

Now, since the negative energy of the fundamental orbit is equal to the work of ionization of the atom (see **310**, conclusion), according to Eq. (258a) an electron, after passing through a potential difference of $E = \frac{6.87 \cdot 10^{-12}}{1\,591 \cdot 10^{-20}} = 4.32 \cdot 10^{8}$ abs. units =

4.32 *volts*, must have sufficient energy to ionize the potassium atom; the observed value for the ionization potential of this element is $E = 4.1$ *volts*.

328. The Shape of the Outer Electron Orbits of the Alkali Metal Atoms.—According to **314**, the shape of an electron orbit is determined mainly by the principal and subordinate quantum numbers.

For the present purposes it is simpler to determine the subordinate quantum number first. Since, according to the selection principle of **318**, the subordinate quantum number can change only by ±1 during electron jumps under normal conditions, the conclusion must be that between the *s*- and the *p*-terms, the *p*- and the *d*-terms, and the *d*- and the *f*-terms the subordinate quantum number increases or decreases by only one unit. This condition is most easily taken care of by setting $n' = 1$ for the *s*-term, $n' = 2$ for the *p*-term, $n' = 3$ for the *d*-term, and $n' = 4$ for the *f*-term. To be sure, if a number of other arrangements were compatible with each condition, they could not be combined with the considerations which follow.

In the simple spectrum of hydrogen, the principal quantum number n could be obtained directly from the magnitude of the term $\Re\frac{Z^2}{n^2}$. In the present case, however, this procedure cannot be applied because the squares of whole numbers are no longer in the denominator. Since from theoretical considerations the quantum number must always be a whole number, the reason for this can only lie in the fact that, while an expression of the form of Eq. (286) is practically suitable for calculating the values of individual terms, it is unsatisfactory in principle. If it is attempted to fit the expression $\Re\frac{Z^{*2}}{n^2}$ to the individual terms, using whole numbers for n, it is found that Z^* varies from term to term. This behavior can be explained directly if it is assumed that the orbits concerned deviate greatly from the circular form; then the orbit will lie partly outside the **kernel** of the atom, and partly penetrate into the kernel also.[1] While over the outer portion of the orbit Z^* has the value of approximately 1, in the inner portion it has considerably larger values and even approaches the full value of Z temporarily. If we follow along the succession of progressive terms in a series, *i.e.*, if n is increased while n' is kept constant, the penetrating part of the orbit is almost unchanged but the outer portion becomes increasingly greater.

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[1] * Bohr calls such orbits *penetrating orbits* (see Fig. 83).

Some idea as to the approximate correctness of this statement can be obtained directly from Fig. 83, if a small circle representing the kernel of the atom is placed about the nucleus and then the courses of the ellipses for which $n' = 1$ are followed. Therefore the average effective nuclear charge Z^* for the total orbit will gradually decrease as the major axis of the ellipse increases (increasing n). Instead of changing the numerator Z^* in $\mathfrak{R}\,\frac{Z^{*2}}{n^2}$ from term to term, it is preferable to keep it constant and therefore change the denominator so that the same object is attained algebraically. *Thus in place of the true principal quantum number n which is always a whole number, an* **effective quantum number** *n^* is introduced; usually this is not a whole number but, similar to n, at least increases by approximately whole numbers.*

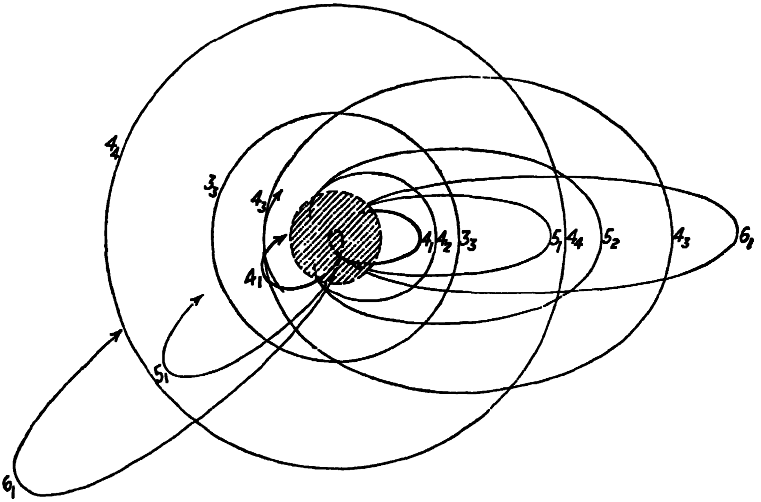

Fig 83

However, not all orbits penetrate into the kernel of the atom, but only those which are elongated, *i.e.*, those for which the subordinate quantum number is relatively small. When the diameter of the kernel is known, it is even possible to state exactly up to which values of n' the orbits will still penetrate. It can be shown that the breadth of the ellipse at the focus, the so-called parameter, depends only upon the subordinate quantum number and therefore upon neither the major axis nor the principal quantum number. By performing this calculation for all the alkali metals except lithium, it was found that only the *s*- and *p*-orbits with the subordinate quantum numbers $n' = 1$ and $n' = 2$ penetrated and the other orbits with greater values of n' revolved around the entire kernel. (In Rb and especially Cs the *d*-orbits approached very close to the kernel.)

On the basis of these considerations it must be expected that in the *s*- and *p*-orbits Z^* (if n is a whole number) will vary considerably or that there is a large difference between n and n^* for a definite, constant value of Z^*, while in the *d*- and *f*-orbits Z^* is always approximately equal to 1, and n^* must be nearly the same as n. In this way we obtain directly from the above formulas for the series of the potassium spectrum, $n = 4$ for the smallest *f*-orbit as well as $n = 3$ for the smallest *d*-orbit (final orbit of the Bergmann series). These orbits are, therefore, represented by $n_{n'} = 3_3$ and $n_{n'} = 4_4$, and are circular

For the penetrating orbits the true quantum number n must be determined by calculation from the terms of the spectral lines or from n^*, but the exact calculation of this number is still prevented by a number of difficulties, of which those mentioned at the end of **321** are particularly important. Yet from the calculations made up to the present[1] it seems probable that the smallest *s*-orbit (the normal orbit of the outer electron) as well as the smallest *p*-orbit has the principal quantum number $n = 4$. This result, which is still somewhat uncertain, will be confirmed by the considerations in **347**, according to which the principal quantum number of the normal orbit is increased by one unit in the alkali metals following in the order of the periodic system; from this we find for Li, $n = 2$; for Na, $n = 3$; for K, $n = 4$, etc.

In this way a quite considerable difference is obtained between the true and the effective quantum numbers; for the *s*-terms of potassium the difference is about 2.299; for the *p*-terms, 1.7652 or 1.7682.

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[1] SCHRÖDINGER, E., *Z. Physik*, **4**, 347 (1921); FUES, *ibid*, **11**, 346; **12**, 1 (1922); VAN URK, *ibid.*, **13**, 268 (1923).

Although the normal orbit of potassium is to be designated by the quantum number 4_1 as a first approximation,[1] the actual electron orbit differs rather considerably from a normal 4_1-ellipse such as is found in the hydrogen atom. It must first be noted that the effective nuclear charge *on the average, i.e.,* taking into consideration the inner portion of the orbit, is greater than unity; therefore the average (negative) orbital energy is appreciably greater and the greatest distance between the electron and the nucleus is smaller than in a 4_1-ellipse in the hydrogen atom. A very marked precession is also characteristic of the motion. This happens because the electron temporarily comes very close to the nucleus; at this moment the full nuclear charge acts on it, causing such a strong deflection that a relatively very sharp turn around the nucleus takes place. In the sense of **314** the strong precessional motion is formally explained by saying that as the result of the variation in Z^* the force really acting upon the electron from point to point no longer follows Coulomb's law. A schematic representation of the outer electron orbits of potassium is given in Fig. 83; the region of the inner electrons is indicated by the shaded circular area.

It is impossible here to enter into the consideration of the previous attempts to explain theoretically the fine-structure of numerous terms and spectral lines (doublets, etc.); in order to describe them formally, it is necessary to introduce one further (inner) quantum number, just as with the X-ray spectrum.[2]

329. The Spectral Displacement Law.—In **319** it was shown that for the singly charged, ionized helium atom (spark spectrum) we had the same spectral formula as for the neutral hydrogen atom (arc spectrum), except that a factor 4 was introduced on account of the double charge on the nucleus, and the value of the Rydberg constant was slightly different. This result was generalized by Sommerfeld and Kossel (1919) and stated as the **law of spectral displacement:** *The arc spectrum emitted by a neutral atom shows a far-reaching similarity to the first spark spectrum of an atom with an atomic number one unit higher, and with the second spark spectrum of an atom two units higher.* This similarity becomes particularly striking when the terms of the first spark spectrum are multiplied by 4 and those of the second by 9. An example of this is given in the following formulas which hold to some degree of approximation for the sharp series:

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[1] Corresponding to this result it is appropriate to introduce the true quantum number into the method of notation, *e.g.*, for the principal series of potassium we shall not write as previously $(1, s) - (m, p)$ with $m = 2, 3, 4 \ldots$ but $(4, s) - (m, p)$ with $m = 4, 5, 6$ (See PASCHEN, F., *Ann. Physik*, **71**, 142 (1923).)

[2] * For information on these matters the student should consult SOMMERFELD, *loc. cit.*, p. 358 *et seq.*

Arc spectrum of Na:

$$v' = \mathfrak{R}\left(\frac{1}{\left(3 - \begin{Bmatrix}0.89\\0.90\end{Bmatrix}\right)^2} - \frac{1}{(m - 1.38)^2}\right)$$

First spark spectrum of Mg:

$$v' = 4\mathfrak{R}\left(\frac{1}{\left(3 - \begin{Bmatrix}0.735\\0.737\end{Bmatrix}\right)^2} - \frac{1}{(m - 1.08)^2}\right) \qquad m = 4, 5, 6 \ldots$$

Second spark spectrum of Al:

$$v' = 9\mathfrak{R}\left(\frac{1}{\left(3 - \begin{Bmatrix}0.627\\0.629\end{Bmatrix}\right)^2} - \frac{1}{(m - 0.91)^2}\right)$$

Not only the general displacement law but also the manner in which the differences between the true and effective quantum numbers change is in excellent agreement with the ideas of atomic structure developed up to the present time. The spectrum depends mainly upon the effective nuclear charge of the outer portion of the orbit; this increases from the arc spectrum to the first and second spark spectra in the ratio 1 to 2 to 3; therefore, according to Eq. (283), the factors by which the Rydberg constant must be multiplied are 1, 4, 9.

However, the changes in the effective nuclear charge, which occur when an electron enters into the interior of the atom and whose effect may be expressed as the difference $n - n^*$ in the quantum number, become greater on a percentage basis when the effective quantum number is lowered from its relatively high, approximately constant value over the inner portion of the orbit to the value 1 in the outer portion than when it drops only to 2 or 3. Actually, the above formulas show directly that the difference $n - n^*$ becomes smaller from the arc spectrum of Na to the second spark spectrum of Al.

330. The Spectra and the Atomic Structure of Helium.—Besides the spark spectrum mentioned in **319,** helium also has two arc spectra which differ considerably from each other and never show transitions from one to the other, *i.e.*, do not have terms in common. It was quite soon concluded that *there must be two modifications of helium, "parahelium" and "orthohelium."* While the spectrum of parahelium has a series which lies in the ultra-violet region and has a one-quantum limiting term just as the Lyman series of hydrogen, the largest term of orthohelium corresponds to the quantum number 2. Since in absorption spectra ordinary helium shows only the shortest wave-length series of parahelium with the quantum number of the limiting term $n = 1$, the parahelium modification is the normal state. The orthohelium modification can thus exist only in the excited state; in order to produce this from the normal state of parahelium requires more powerful influences than an energy addition by means of radiation represents, *e.g.*, orthohelium forms by collisions with electrons which have passed through a potential difference of not less than 19.75 *volts.* Moreover, it follows from the behavior of orthohelium (*e.g.*, as compared with the impurities in the helium used for investigation) that a chemical activity must be ascribed to it similar to that of an alkali metal atom; therefore in this modification the helium atom has entirely lost the character of an inert gas. In view of this it is noteworthy that in every respect the spectrum of orthohelium is similar to that of lithium.

The difference between the spectra and other properties of para- and orthohelium leads to the conclusion that the electron configurations of the two modifications must be entirely different. However, the possibility of a fundamental difference consists only in *a difference in the spatial arrangement of the two electron orbits.* It is, therefore, concluded that in the one modification both orbits lie in the same plane, but in the other they are crossed.

The results of calculations indicate with certainty that *in orthohelium both orbits are in the same plane and that the crossed orbits must be assigned to parahelium.* This may be seen most easily from the fact that the difference $n - n^*$ for corresponding orbits, such as the elliptical 2_1-orbit, is greater in the ortho than in the para modification. If both orbits lie in the same plane, the outer electron moving on a 2_1-orbit will, on the average, approach closer to the inner (1_1-) electron than in crossed orbits; therefore, in the first case the outer orbit will exhibit the character of a penetrating orbit to a higher degree and thus a greater apparent diminution of n than in the second.

f. THE SPECTRA OF MOLECULES[1]

α The Rotation Spectrum

331. Application of the Frequency Law to the Radiation of Rotating, Polar Molecules.—From the classical as well as the newer theory it is to be expected that rotating molecules *(rotors)* consisting of atoms with polar electric charges should send out electromagnetic waves similar to those sent out by electrons rotating around a nucleus. A spectrum from molecules can, indeed, be observed in the infra-red region which without doubt is due to these rotational motions and is, therefore, called the **rotation spectrum.**

Now while, according to classical theory, all possible rotation frequencies are permissible, an application of the results obtained for the electronic motions in the interior of the atom would suggest that the rotor can, in general, assume only definite, *stable*, energy values[2] and that an interaction between radiation and a rotor can occur only when its energy changes discontinuously. The frequency of an absorbed or emitted wave corresponding to an energy change of the magnitude $U_1 - U_2$ is again determined by the frequency law. In contrast to the oscillator and the freely rotating electron, the (rigid) rotor possesses only kinetic energy.

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[1] For general articles on this subject see EUCKEN, A., *Jahr Radioakt, Elektronik*, **17,** 361, 1920; KRATZER, A., *Ergebn. exakt. Naturwissenschaften*, **1,** 315 (1922); *SOMMERFELD, *loc cit*, chap VII.

[2] That the rotational energy of the molecule is really distributed in energy quanta could have been inferred from the decrease of the molecular heat of hydrogen at low temperatures (see **52**).

For the total energy U_r of a stable (non-radiating) rotational movement, we can, therefore, set

$$U_k = U_r = \frac{n'h\mu}{2} \quad (n' = 1, 2, 3 \quad .), \tag{287}$$

which is similar to Eq. (273).

In order to obtain a convenient expression for the rotation spectrum with the help of Eqs. (287) and (267), it is expedient to consider the general (mechanical) equation for the energy of a rotor which will introduce the moment of inertia J into the calculation. Thus,

$$U_r = \frac{J}{2}\omega^2 = \frac{J}{2}(2\pi\mu)^2. \tag{288}$$

Now from Eqs (287) and (288) either μ or U_r can be eliminated and the following obtained

$$\mu = \frac{n'h}{4\pi^2 J}$$

$$U_r = \frac{n'^2h^2}{8\pi^2 J}. \tag{289}$$

The amount of energy which a rotor can take up does not, therefore, increase linearly as for a Planck oscillator (Eqs. (94) and (99)), but as the square of the quantum number n'.

The application of the frequency law gives the following for the rotation spectrum:

$$h\nu = U_1 - U_2 = \frac{h^2}{8\pi^2}\left(\frac{n_1'^2}{J_1} - \frac{n_2'^2}{J_2}\right) \tag{290}$$

In case the molecule is not quite rigid, it is to be expected that, as a result of the centrifugal force, the moment of inertia will increase as the velocity of rotation (quantum number) increases, and that, therefore, J_1 and J_2 are somewhat different. In some cases, especially diatomic molecules, the difference seems to be trifling, so that it may be neglected[1] Then,

$$\nu = \frac{h}{8\pi^2 J}(n_1'^2 - n_2'^2). \tag{290a}$$

Since in this case there is a harmonic circular motion, the quantum number can only be changed by one unit (see **318**); therefore

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[1] Concerning an exception for the CO_2 molecule, see EUCKEN, A., *Z. physik. Chem*, **100**, 161 (1922).

$n_1' = n_2' + 1$. In other words, only waves with the frequencies which satisfy the following relation will be emitted or absorbed:

$$\nu = \frac{h}{8\pi^2 J}(2n_2' + 1) = \frac{h}{4\pi^2 J}\left(n' + \frac{1}{2}\right) \qquad (n' = 0, 1, 2, 3 \ . \ . \ .). \qquad (290b)$$

According to this, *the rotation spectrum consists of a number of sharp lines with a constant interval* $\frac{h}{4\pi^2 J}$ *between them.*

Up to the present only in one case, that of water vapor, has even a part of the rotation spectrum been accurately measured.[1] It was shown that in the long-wave-length infra-red region of the spectrum, water vapor possessed a number of sharp absorption lines between 9 and 300μ, through which the discontinuous character of the rotation spectrum demanded by the quantum theory was directly confirmed.

TABLE 75.—ROTATION SPECTRUM OF WATER VAPOR BETWEEN 50 AND 300μ

n'	λ calc.	λ obs.
2	237	256
3	169	175
4	131 5	132
5	107 5	105 8
6	92	91
		83
7	79	78
8	69 7	72 2
9	62 5	65 8
10	57 7	56 5

In the application of Eq. (290*b*) to these measurements, it is to be noted that a triatomic molecule, such as water, can perform rotation about three axes and consequently must have three principal moments of inertia so that the observed rotation spectrum probably consists of three superimposed series of the type of Eq. (290*b*) or of the type of Eq. (290*a*) if the molecule is not sufficiently rigid. As Table 75 shows, the lines observed between

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[1] RUBENS, H , *Berl. Akad Ber.*, 8 (1921); this gives references to the previous literature. * Also see LEWIS, W. McC., *loc. cit.*, 3, p. 85.

50 and 200μ all appear to belong to *one* series, which, corresponding to Eq. (290*b*), may be satisfactorily represented by the formula $\frac{1}{\lambda} = \nu' = \frac{n + \frac{1}{2}}{0.0591}$ cm^{-1}. This gives a moment of inertia amounting to $3.2 \cdot 10^{-40}$ *g. cm.*^{2}

A strong absorption in the long-wave infra-red region can also be demonstrated for several other polar gases (*e.g.*, HCl gas). These are undoubtedly due to the rotation spectrum but the individual lines have not yet been measured.

β The Motion of the Nuclei in Molecules

332. The Vibration Spectrum.—As has already been noted in **52,** it is necessary to assume that the atoms in a molecule are not bound to each other with complete rigidity, but that oscillations with respect to each other occur. In the case of atoms bearing polar charges, the presence of these oscillations is shown directly by electromagnetic waves; in general, *these waves lie in the short-wave-length portion of the infra-red spectrum.*

Besides a fundamental vibration for which the energy may be represented by U_{0s}, there also exists a vibration spectrum for which, as far as can be determined at the present time, the formula for a Planck oscillator (**72**) holds as a first approximation:

$$U_s = n'' U_0. \tag{291}$$

This formula states that the energy value of the various vibrating states increases proportionally to the quantum number n''.[1] A more accurate representation of the facts is obtained by adding a term in the second degree (the so-called *anharmonic oscillator*), with the result that

$$U_s = n'' U_0 + an''^2. \tag{291a}$$

The application of the frequency law gives for the frequency of the emitted or absorbed radiation

$$\nu = \frac{U_0}{h} (n_1'' - n_2'') + a(n_1''^2 - n_2''^2). \tag{292}$$

Thus the vibration spectrum, similar to the rotation spectrum, appears as a number of nearly equidistant lines; while for pure harmonic oscillators only quantum jumps of one unit can occur, in anharmonic oscillators all jumps are possible, due to the presence of the overtone vibrations (see **318**).

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[1] This quantum number n'' is not the same as the "equatorial" quantum number of **316** *et seq.*

As yet, only a few (two or three) lines at the beginning of the vibration spectrum have been directly measured, *i.e.*, only those lines for which the energy changes correspond to a few units and whose wave lengths, as Eq. (292) demands, are proportional to small whole numbers. For example, HCl gas shows absorption lines at 3.46 and 1.76μ; HBr at 3.91 and 1.98μ; CO at 4.67 and 2.35μ; HCN at 14.14 and 7.08μ; water vapor at 6.26, 3.15, 2.02, 2.66, 1.37, 0.9, and 0.69μ; in the last case the vibration spectrum is resolved into several series on account of the greater number of degrees of freedom, but only Eq. (292) is required to represent each series.

333. Combination of the Vibration and Rotation Spectrum.—In general, the vibration spectrum does not occur alone but combined with the rotation spectrum. In the light of Eq. (267) this means that, simultaneous with the emission of rotational energy, an emission of vibrational energy also occurs, using the terms "rotation" and "vibration" in the sense of the two preceding paragraphs. On this account a number of new waves are obtained whose frequencies are given by the *total* energy difference of the system before and after emission:

$$\nu = \frac{U'_1 - U'_2}{h} = \left(\frac{hn'^2_1}{8\pi^2 J_1} + \frac{U_0 n''_1}{h}\right) - \left(\frac{hn_2'^2}{8\pi^2 J_2} + \frac{U_0 n''_2}{h}\right). \quad (293)$$

or if, on account of the harmonic character of the rotation which limits the quantum jumps to one unit at a time, we put $n'_1 = n'_2 \pm 1$, and further

$$\frac{U_0(n''_1 - n''_2)}{h} = \nu_0,$$

we get

$$\nu = \nu_0 + \frac{h}{8\pi^2 J_1} \pm \frac{hn'_2}{4\pi^2 J_1} - \frac{hn'^2_2}{8\pi^2}\left(\frac{1}{J_2} - \frac{1}{J_1}\right). \quad (293a)$$

The first term ν_0, which is due to the vibration, is usually considerably larger than the remaining ones due to the rotation. Therefore a whole series of vibrations are obtained on both sides of ν_0 which lie rather close together, so that, as a whole, one gets the impression of a double band consisting of a number of sharp lines. For the separation $\Delta\nu$ of two neighboring lines, disregarding the term involving n'^2, we obtain as a first approximation

$$\Delta\nu = \frac{h}{4\pi^2 J_1}. \quad (293b)$$

These same differences are obtained according to Eq. (290*b*) for the rotation spectrum; it follows, therefore, that the rotation spectrum has been projected to a certain degree from the long-wave infra-red region of the spectrum into the short-wave region, so that it is possible to study its structure from measurements in the relatively short-wave-length region even when the long-wave-length region cannot be attained experimentally.

Equation (293*a*) has been qualitatively confirmed by experiment. In the rougher observations the intramolecular vibrations do not appear as individual sharp lines but as broad double bands, as is illustrated in Fig. 84 (for HCl). With better experimental means, these bands can be resolved into a number of sharp lines. An illustration of this is given in Fig. 85, from which may be seen the absorption band of HCl at 3.46μ as it appears after a more powerful resolution of the lines.[1] It is remarkable that no wave of the fundamental frequency ν_0 is present. Moreover, this could not lie halfway between the two strongly marked lines on the right and left of the gap, but, on account of the term $\frac{h}{8\pi^2 J_1}$, it must be displaced by $\frac{\Delta\nu}{2}$. Besides the fundamental vibration there is also lacking, as Fig. 85 shows, one other whose frequency corresponds either to the transition $n'_1 = 1$, $n'_2 = 0$ or $n'_1 = 0$, $n_2' = 1$. As a result of the squared term, the interval between the lines is not quite constant, but increases with the wave length. In the immediate

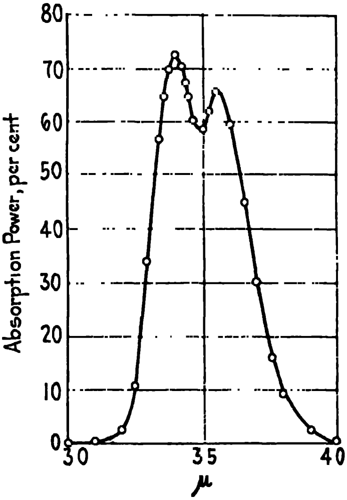

FIG. 84

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[1] IMES, E. S., *Astrophys. J.*, **50**, 251 (1919).

vicinity of the zero line the influence of this term is small and therefore the moment of inertia J_1 of the molecule in the normal state can be calculated from Eq (293*b*). Values for several molecular moments of inertia calculated in this way are found in Table 76, column 3.

Just as with the rotation spectrum, the relations for tri- and polyatomic molecules are more complicated than for the diatomic molecules, since the various series of the rotation spectrum must also be picked out from the fine-structure of the double bands.

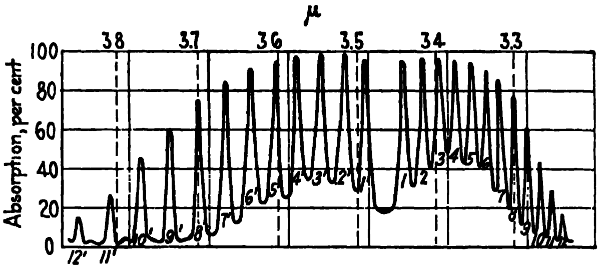

Fig 85

334. The Infra-red Double Bands from the Standpoint of the Classical Theory.—It is noteworthy that the combination of an inner vibration of frequency $\nu_0 = \mu_0$ with a rotation frequency $\nu_r = \mu_r$ can be understood from purely classical theory without the use of the quantum relation (Eq (293)) Consider a tuning fork which vibrates with the frequency ν_0, and at the same time revolves rapidly (number of revolutions equal ν_r); then "beats" of the frequency ν_r arise from the tone of frequency ν_0 The same beats may be produced from two differently tuned forks of the frequencies

$$\nu = \nu_0 \pm \nu_r.$$

Thus, in case a molecule sends out an inner vibration ν_0 and at the same time rotates with the mean frequency ν_{rm} (the structure of the rotation spectrum may be disregarded at this point) then there is obtained in place of ν_0 the two frequencies $\nu_0 \pm \nu_{rm}$. For the distance between the two lines we have $\Delta\nu = 2\nu_{rm}$. Now the mean velocity of rotation (or, more accurately, the root mean square of the velocity) is related to the mean energy of a rotor in a simple way as the result of Eq. (287) and

$$U_r = \frac{J}{2}(2\pi\nu_{rm})^2.$$

At higher temperatures the law of energy partition holds approximately for the present purpose, and since we are concerned with two degrees of freedom it follows that

$$U_r = kT = \frac{J}{2}(2\pi\nu_{rm})^2. \tag{294}$$

This equation, derived without the introduction of quanta, permits the calculation of the molecular moment of inertia from the mean distance of the double bands *which have not been resolved into their fine structures.* In its application it is to be observed that the term ν_{rm} does not coincide with the most frequently occurring rotation velocity, ν_{rh}, *i.e.*, with the vertex of the curve in Fig. 84 It is given by an equation similar to Eq. (82*b*) (see **48**), viz. $\nu_{rm} = \sqrt{2}\nu_{rh} = \frac{\Delta\nu_{rh}}{\sqrt{2}}$, where $\Delta\nu_{rh}$ represents the distance between the maxima of the double bands. The moment of inertia of a molecule is thus given by

$$J = \frac{kT}{\Delta\nu_{rh}^2\pi^2}. \tag{294a}$$

For HCl gas where the maxima of the double bands lie at $\lambda_1 = 3.55\mu$ and $\lambda_2 = 3.40\mu$, we obtain

$$\Delta\nu_{rh} = \frac{V_l}{\lambda_2} - \frac{V_l}{\lambda_1} = (0.883 - 0.845)10^{14} = 3.8 \cdot 10^{12},$$

and therefore

$$J = \frac{1.37 \times 10^{-16} \times 300}{14.5 \times 10^{24} \times 10} = 2.8 \cdot 10^{-40}.$$

TABLE 76.—MOLECULAR MOMENTS OF INERTIA OF DIATOMIC GASES

Gas	Moment of inertia $J \cdot 10^{40}$ ($g.$-cm^2) Equation (294*a*), distance between infra-red double bands	Equation (293*b*), distance between lines in infra-red bands	Equation (296*a*), band spectrum	Distance between atomic nuclei $d \cdot 10^8$ *cm.*
N_2			14.2	1.12
CO	14.7		15.8	1.16
O_2			9.5	0.85
HBr	3.6	3.27		1.42
HCl	2.8	2.64		1.28
HF		1.37		0.94

A few other results for the moment of inertia obtained in this way are given in Table 76, column 2.

The distance d between the two atomic nuclei may be found without difficulty by means of the formula

$$J = \frac{m_1m_2}{m_1 + m_2}d^2 = \frac{A_1A_2d^2}{N(A_1 + A_2)}.$$

For example, for HCl (with $J = 2.64 \cdot 10^{-40}$, $A_1 = 1$, $A_2 = 35.5$)

$$d = \sqrt{\frac{1.60 \cdot 10^{-16} \cdot 36.5}{35.5}} = 1.28 \cdot 10^{-8}\ cm.$$

γ Electron Vibrations (Band Spectra)

335. Electron Transitions within the Molecule.—In molecules also, there occur transitions of certain electrons from one orbit to another which result in the emission or absorption of radiant energy. That the characteristic radiation of a molecule can be due only to the outer electrons and must, therefore, lie in the vicinity of the visible spectrum is clear since the interior of the atom is not affected by the formation of molecules. Concerning the arrangement of the spectral lines sent out by these electrons, existing knowledge is very incomplete; yet it is sufficient to establish that for them, just as for the electrons in the atom, a number of stable orbits (without radiation) will exist. The energy of these orbits may be designated by $f(n)$; then a transition from orbit 1 to orbit 2 emits a wave of frequency

$$\nu = \frac{1}{h}f(n_1) - \frac{1}{h}f(n_2). \qquad (295)$$

336. Origin and Structure of Band Spectra.—The radiation caused by the electron transitions within the molecule never occur alone, but are always combined with the rotation and atomic vibration spectrum just as the last two always occur together. For the frequency of such as oscillation we obtain, similar to the above,

$$h\nu = \underbrace{\underbrace{f(n_1) - f(n_2)}_{\nu_{01}(\text{ELECTRONS})} \pm \underbrace{(U_{s1} - U_{s2})}_{\nu_{02}(\text{ATOMIC VIBRATION})}}_{\nu_0} \pm \underbrace{(U_{r1} - U_{r2})}_{(\text{ROTATION})}. \qquad (296)$$

In this $U_{s1} - U_{s2}$ is to be replaced by Eq. (291a), and $U_{r1} - U_{r2}$ by Eq. (290).

Altogether, we are confronted with three sets of quantum transitions, corresponding to the electron transitions (n_1, n_2), the atomic vibrations (n''_1, n''_2), and the rotation (n_1', n_2'). It is clear that such a spectrum, which from its appearance is called the *band spectrum*, has an extraordinarily complicated structure.

The entire band spectrum of a molecule resolves first into a series of different *band groups*, which frequently are not to be observed simultaneously, but appear separately depending upon the conditions of excitation. A definite electron transition

$f(n_1) - f(n_2) = \nu_{01}$ corresponds to each band group. Nitrogen has six band groups, the violet cyanogen band, the red cyanogen bands, the first, second, and third positive groups, and one negative group. The first two have been erroneously ascribed to cyanogen; the positive groups receive their name from the circumstance that in the Geissler tube they are observed especially in the vicinity of the anode; and the negative group is found near the cathode.

337. The Structure of the Individual Band Groups.—Each individual band group resolves into a number of individual bands, as is shown in the positive band spectrum of nitrogen partially reproduced in Fig 86, page 502. The exact position of a band is indicated by means of the null frequency

$$\nu_0 = \nu_{01} + U_{s1} - U_{s2},$$

i e, the frequency for the state in which no rotation occurs. Now if the expression Eq (291*a*) is substituted for U_{s1} and U_{s2}, it is to be noted that after an electron transition the whole inner structure of the molecule will be changed, since the constants U_0, and a of Eq (291*a*) have been involved; before and after the electron transition there are two different modifications of the molecule For the null frequency ν_0 of a single band we have

$$\nu_0 = \nu_{01} + U_{01}n''_1 + a_1n''^2_1 - U_{02}n''_2 - a_2n''^2_2$$

As Heurlinger[1] has shown, in many cases all the null lines of the band spectrum can be fitted into this formula, *i e*, all the null lines can be resolved into the two series if in the one series n''_1 is constant and n''_2 variable while in the other series n''_2 is constant and n''_1 variable

338. The Structure of the Individual Bands.—The individual bands consist of a number of closely neighboring lines, all of which correspond to a definite electron transition and a definite change of atomic vibration but different transitions in the rotational energy (n'_1 and n'_2)

If we combine the first two terms of Eq (296) and, simultaneously, the expression already given in Eq (293*a*), $\frac{h}{8\pi^2J_1}$, in the term ν_0, then we obtain for the line sequence of a band the formula

$$\nu = \nu_0 \pm \frac{h}{4\pi^2J_1}n' + \frac{h}{8\pi^2}\frac{(J_1 - J_2)}{J_1J_2}n'^2. \qquad (296a)$$

According to this, there are two branches of the band, one on each side of ν_0, corresponding to the positive and negative signs This is similar to the infra-red double bands. On account of the second-degree term of n', the two branches proceed in opposite directions only for small values of n', where the term involving n'^2 becomes small; for larger n' values the negative branch reverses its sign (it then depends only on the squared term), so that both branches proceed in the same direction Near the inversion point, the so-called *head of the band*, the lines accumulate.

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[1] *Z. Physik.*, **1**, 88 (1920).

According to the above the head of the band has no theoretical significance (the frequency number ν_0, in general, lies some distance away from it). Since the lines of a single band lie so close together, especially near the head, it is clear that the disentanglement of such a band involves considerable difficulties. Moreover, it often happens that, in addition to the two branches already mentioned, there is also a third one for which the linear term in the equation is lacking; this branch is thus produced by an electron transition when the energy of rotation is constant ($n'_1 = n'_2$) but for which the moment of inertia changes because of the change of the inner grouping of the molecule

As far as the band spectrum has been resolved up to the present, the observations may be represented fairly well by Eq. (296*a*). One can, therefore, attempt to use the linear term involving n' for the calculation of the molecular moment of inertia J_1. For CO it is possible to compare the moment of inertia thus found with the value found by other methods; the result is quite satisfactory. A few other values for the moment of inertia of diatomic gases calculated from the band spectra are also given in Table 76, column 4.

339. The Significance of the Band Spectra in the Theories of Molecular Structure.—When light of short wave length is emitted or absorbed as the result of electron transitions inside a molecule, the explanation of both the rotation and the vibration spectrum is obtained at the same time. Just as the rotation spectrum becomes superimposed upon the atomic vibration spectrum, the present case may be considered as a projection of both spectra into the electron spectrum. It is worth noting that these phenomena no longer involve the condition of polar atomic charges, but that the motion of non-polar molecules is also represented in all details in the short-wave-length band spectrum.

Since the band spectrum reveals all the possible energy transitions within a molecule, it represents an extremely valuable physical means for investigating the constitution of molecules.

One of the most important general results following directly from a study of the band spectrum is that the molecule is quite similar to the atom in being capable of existing in a large number of states. The number of these states, even for the simpler molecules, appears to be considerably greater than in atoms, as is shown by the complicated structure of the band spectrum. The quantitative investigation of the band spectrum involves great difficulties. The first attempt is to "disentangle" the spectrum, *i.e.*, to find the lines belonging to a single series and to fit the observations to Eq. (296*a*). Happily, it is now feasible, as Wood has shown, to excite under certain conditions only single lines (closely related lines, *e.g.*, those belonging to definite n'_1, and n''_1, values) as fluorescence lines, by which the unraveling of the complicated band spectra is remarkably facilitated and in many cases is made possible for the first time.

A problem which involves a complete analysis of the band spectrum would be the search for a model of the molecule which corresponds to the band spectrum, just as Bohr succeeded in finding the model of the hydrogen atom from the Balmer series. There can thus be no doubt that the investigation of the band spectra promises to be of great importance for chemical problems.

g. THE LAW OF BLACK-BODY RADIATION[1]

340. The Hollow Body as an Ideal Source of Black-body. Radiation.—The line spectra of atoms and the band spectra of molecules stand out sharply (except the X-ray spectra) only if the material is subjected to the action of radiant energy while in a very dilute gaseous state. Even the gases at higher pressures give broad and indistinct lines, while in the liquid and solid states the individual differences between spectra, with but few exceptions, become still less definite; generally, only broad, vaguely defined spectral regions in which absorption or emission occurs are found.

For a number of solid substances the individual differences are so nearly completely wiped out that a general law for the spectral distribution of the radiated energy is obtained which has the character of a limiting law. Since this same law is obtained in a more general form for the free radiation from materials which are called "optically black" (soot, platinized platinum, etc.) than for other substances, it is generally called the **law of black-body radiation.**

As an ideal black body, for which the limiting law for black-body radiation is completely fulfilled, a hollow opaque body (*Hohlraum*) with a large surface, but of any shape, from which the radiation can issue through a very small opening can be used.

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[1] PLANCK, M., "Theory of Heat Radiation," translated by M. MASIUS, Blakiston, Philadelphia (1914). * LEWIS, W. McC., *loc. cit.*, vol. 3, chap. II *et seq.*

The reason why in a hollow body all individual characteristics of the walls are eliminated and the original radiation is "purified" is based upon a law announced by Kirchhoff, according to which the ratio of the power of emission to that of absorption depends only upon the wave length and temperature and is the same for all bodies. If, therefore, a certain form of radiation (wave length) in a hollow body of uniform temperature is especially strongly emitted, the same radiation will also be very strongly absorbed and thus cannot exceed a certain limit inside the hollow body. Conversely, a radiation whose wave length is but seldom emitted is only slightly absorbed during its passage through the hollow body and may thus be strengthened until the absorption, which likewise is increasing (in per cent), sets a limit to this increase. The hollow-body radiation is no longer dependent upon the number of particles (oscillators) emitting at various wave lengths; it is just as if exactly the same number would have been present from all the oscillators of different wave lengths. As a result of this compensating action of the hollow body, not only the number but also the other special characteristics of the oscillators become of minor importance, so that one needs only relatively simple (schematic) assumptions about the oscillators in order to understand the theoretical significance of the law of black-body radiation.

341. Definitions.—While for the line and band spectra the intensity of the individual lines is of but slight interest in comparison with their wave lengths, these intensities are of prime importance for the law of black-body radiation.

In order to be able to express the *intensity of a radiation* in a formula, an exact physical definition of this concept is necessary. The total intensity of radiation S is understood to be the amount of (spectrally unresolved) energy which is radiated from 1 $cm.^2$ of the surface of the radiating body or hollow body over a space angle of 1 in unit time and at right angles to the surface. For the monochromatic radiation intensity E_λ, a cross-section of the width $d\lambda = 1$ of the spectrum is considered. Therefore, a body with the surface q would radiate in the time t in a width $d\lambda$ of the spectrum in a definite space angle $d\psi$ perpendicular to the surface an amount of energy

$$U = E_\lambda \cdot q \cdot t \cdot d\psi \, d\lambda.$$

If the color of the light is expressed in terms of the frequency $\nu = \frac{\mathsf{V}_l}{\lambda}$ instead of the wave length, then

$$U = E_\nu q \cdot t \cdot d\psi \, d\nu,$$

in which E_ν is not the same as E_λ, the relation between these two terms being given by $E_\lambda = \frac{\mathsf{V}_l E_\nu}{\lambda^2}$, since $d\nu = -\frac{\mathsf{V}_l d\lambda}{\lambda^2}$.

Besides the intensity of the radiation S or E_ν, the conception of radiation density is also indispensable for radiation theory. Inside a hollow space filled with radiation, a certain amount of energy is stored at every instant, namely, that energy which is under way (flowing) due to the mutual radiating of the walls. Just as material bodies possess a certain heat content, so must a certain amount of radiant energy be ascribed to the hollow space which is thought of as free from matter. The energy content of 1 *cm.*^{3} of the hollow space is nothing other than this **radiation density.** By spectral analysis we get the idea of a monochromatic radiation density u_ν, which is related to the intensity of radiation E_ν or E_λ of the hollow body by the simple expression

$$u_\nu = \frac{8\pi E_\nu}{\mathsf{V}_l} = \frac{8\pi\lambda^2 E_\lambda}{\mathsf{V}^2_l}. \tag{297}$$

342. Empirical Results.—The law of black-body radiation thus consists in a statement concerning the dependence of the radiation intensity E_λ of a definite wave length, or of the radiation density u_ν, upon (1) the temperature and (2) the wave length or frequency.

In the experimental determination of this dependence, it is expedient to vary only one of these two variables at a time. If the radiation sent out by a black body is analyzed by means of a prism or other spectral methods, it is possible to observe a certain color and follow its change of intensity as the temperature is varied (*isochromatic method*). The experimental results of such an investigation, using several wave lengths, is given in Fig. 87.

If the temperature is fixed and the intensities of the different lines (colors) are measured over the whole spectrum (*the isothermal method*), a family of curves like those in Fig. 88 is obtained according to the measurements of Lummer and Pringsheim; these pass through a decided maximum which is displaced towards the shorter wave lengths as the temperature increases.

The behavior of the isochromates as well as the isotherms may be represented by the following formula, which was found empirically by Planck (1900) and later given an exhaustive theoretical foundation:[1]

$$E_\lambda = \frac{c_1}{\lambda^5} \cdot \frac{1}{e^{\frac{c_2}{\lambda T}} - 1}. \tag{298}$$

It has recently been satisfactorily confirmed by the measurements of H. Rubens and G. Michel.[2] The two constants c_1 and c_2, according to the new measurements, have the values $c_1 = 5.89 \cdot 10^{-6}$ *erg cm.*^{2} *sec.*$^{-1}$, $c_2 = 1.430$ *cm. deg.*

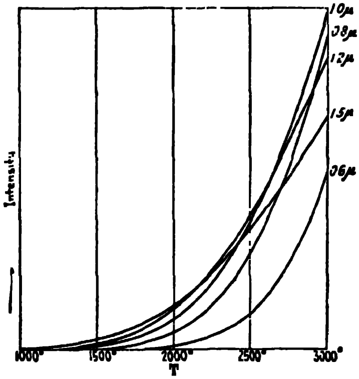

FIG. 87.

Upon differentiating E_λ with respect to λ (T is kept constant) and equating to zero, the maximum λ_m of the isotherm is found always to be at $\frac{c_2}{\lambda_m T} = 4.9651$, *i.e.*, $\lambda_m T = \frac{c_2}{4.9651}$.

This regularity (called **Wien's displacement law**) explains why the color of a radiating black body changes, as the temperature is increased, from red to yellow, then to white, and finally to blue. By measuring the color of the intensity maximum, the temperature of the radiating (black) body can be determined, although not very accurately.

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[1] On the basis of general (thermodynamic) considerations, W. Wien as early as 1893 had found that the radiation law must have the general form $E_\lambda = \frac{1}{\lambda^5}F(\lambda T)$ (*Wien's radiation law*).

[2] *Berl. Akad. Ber.*, 590 (1921).

The total radiation S sent out by a black body is obtained by integrating $E_\lambda d\lambda$ over all wave lengths at constant temperature. This gives the simple formula

$$S = \sigma T^4, \tag{299}$$

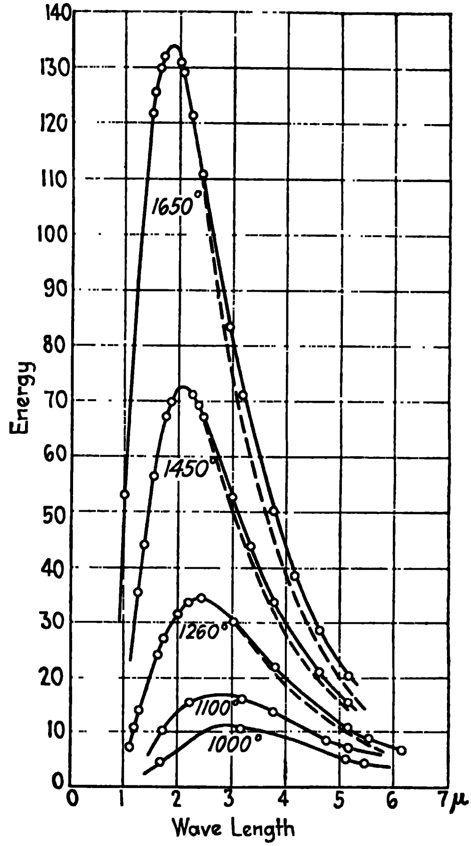

FIG 88.

which was first found empirically by Stefan (1879) and later was given a theoretical basis independent of Planck's radiation law by Boltzmann (1884). The constant σ is an abbreviation for the expression $\frac{12\pi^5 c_1}{90 c^4_2} = \frac{40.85 \cdot c_1}{c^4_2}$, for which the numerical value[1] is 5.75 *ergs cm.*$^{-2}$ *sec.*$^{-1}$ *deg.*$^{-4}$

343. Derivation of the Law of Black-body Radiation on the Basis of the Einstein Frequency Law.—Einstein has shown (1917) that the law of black-body radiation can be found from the frequency law (Eq. (267)) in a way which has the advantage of not requiring any special assumptions as to the nature of the radiating body. By so doing, this supports the actual relations from the best calculations, since the black radiation of a hollow body is actually quite independent of the material of the radiating body, etc.

The existence of a number of atoms or molecules which are found in the various elementary states (1, 2, 3 n) is assumed Each elementary state will be characterized by its energy, U_1, U_2 . U_n At every transition of an energy state U_1 into a state U_2 a frequency $\nu = \frac{U_1 - U_2}{h}$ will be sent out In order to find out how often (and thus the intensity) a given frequency is emitted, a factor which occurs in the law of black-body radiation, we must first ask how often the energy transition $U_1 - U_2$ will occur But, in order to be able to say anything at all about this last factor, the number Z_1 or Z_2 of elementary states which are characterized by energy values U_1 or U_2 must be known For this the generalized Maxwellian distribution law, as applied in **135**, is assumed [2]

$$Z_1 \text{ or } Z_2 = Z_0 e^{-\frac{U_n}{kT}}.$$

According to Einstein, it is now to be assumed that an elementary state with the energy U_1 passes over spontaneously without any external motive to a state with energy U_2 within a certain time while emitting a radiation; this is similar to a radioactive decomposition of an atom For the number of such transitions dZ_1 from an energy state U_1 to one of energy U_2 the simple Eq (17) holds and thus

$$dZ_1 = k_0 Z_1 dt = k_0 Z_0 e^{-\frac{U_1}{kT}} dt. \qquad (300)$$

On the other hand, a certain influence is established on the energy transitions by means of the radiation field, whose energy density u may amount to u_ν (for the frequency ν). Certain forces will be exerted upon the atom through the field of radiation, by which it will be caused to take up energy at one moment and give up energy at another, due to the purely accidental character of these forces. There exists, therefore, apart from the energy loss which is independent of the radiation and which is expressed by Eq. (300), a certain probability (W_1) on the one side for an energy absorption, and on the other for an energy loss (W_2), due to the influence of the radiation; the probability in both cases is to be considered as proportional to the energy density u_ν of the radiation. For these we obtain:

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[1] Since it is more difficult to measure c_1 directly by experiment than σ, the above value for c_1 is based upon a determination of σ.

[2] Strictly speaking, one more factor p, the "*statistical weight*," which is independent of T, must also be introduced, but this would be eliminated during the latter part of the calculation.

$$W_1 = k_1 u_\nu dt$$
$$W_2 = k_2 u_\nu dt$$

The number of transitions occurring in this way, therefore, amounts to

$$dZ_1' = Z_1 k_1 u_\nu dt$$
$$dZ_2 = Z_2 k_2 u_\nu dt,$$

and the total number of transitions from state 1 to state 2, including both those which have been influenced by radiation and those which have not, is given by

$$dZ_1 + dZ'_1 = dZ_{12} = Z_0 e^{-\frac{U_1}{kT}}(k_0 + k_1 u_\nu)dt$$

and for the reverse process, state 2 to state 1,

$$dZ_{21} = Z_0 e^{-\frac{U_2}{kT}} k_2 u_\nu dt.$$

In the stationary state, for example, where the hollow-body radiation exists in radiant equilibrium with the walls, we must have $dZ_{12} = dZ_{21}$, and therefore

$$e^{-\frac{U_1}{kT}}(k_0 + k_1 u_\nu) = e^{-\frac{U_2}{kT}} u_\nu k_2$$

For u_ν we get first the condition expressed by

$$u_\nu = \frac{k_0 e^{-\frac{U_1}{kT}}}{k_2 e^{-\frac{U_2}{kT}} - k_1 e^{-\frac{U_1}{kT}}}. \qquad 301)$$

Experience shows that at high temperatures where

$$e^{-\frac{U_1}{kT}} \simeq e^{-\frac{U_2}{kT}} \simeq 1$$

the density of the radiation becomes very great. According to Eq (301), this can happen only if the difference $k_2 - k_1$ becomes vanishingly small—therefore, when $k_1 = k_2$ This equation then takes the form

$$u_\nu = \frac{k_0}{k_1} \frac{1}{e^{\frac{U_1 - U_2}{kT}} - 1} = \frac{k_0}{k_1} \frac{1}{e^{\frac{h\nu}{kT}} - 1}. \qquad (301a)$$

In order to express the ratio $\frac{k_0}{k_1}$ in terms of universal constants or ν, it is again necessary to consider the limiting condition for high temperatures and small values of ν, for which Eq. (301a) according to Eq (25) becomes

$$u_\nu = \frac{k_0}{k_1} \frac{kT}{h\nu}. \qquad (301b)$$

In this case the relations are such that the classical theory, *i.e.*, the energy distribution law, can be assumed to hold, this being confirmed by the form of the equation $u_\nu \sim T$.

The way in which a continuum filled with stationary waves is to be treated from the standpoint of the energy distribution law has already been indicated in **76.** To each "vibration possibility," *i. e.*, each wave which can form in the space, one degree of freedom is ascribed. As was first shown by Lord Rayleigh, from such considerations we obtain, according to the classical theory, a formula for the radiation density which in principle is identical with Eq. (301*b*),

$$u_\nu = \frac{8\pi\nu^2}{V_l^3}kT, \tag{301c}$$

and from which by comparison with Eq. (301*b*) it follows that

$$\frac{8\pi\nu^2}{V_l^3} = \frac{k_0}{k_1 h\nu}.$$

Finally, the equation for the radiation density is obtained in the form

$$u_\nu = 8\pi h\frac{\nu^3}{V_l^3}\frac{1}{e^{\frac{h\nu}{kT}} - 1} \tag{301d}$$

344. Planck's Derivation of the Radiation Law.—In a quite different way, Planck (1900) arrived at this equation theoretically by assuming that the walls of the hollow body consist of oscillators whose energy content was represented by Eq. (97*b*). Between the energy of the oscillator and the radiation density u_ν, there is a simple relation which has already been obtained in Eq. (301*c*) as a special case; in the sense of the classical theory the product kT signifies the energy of an oscillator. For a general theory one would therefore put

$$u_\nu = \frac{8\pi\nu^2}{V_l^3}u,$$

where u is the energy of an oscillator. If the value of u found in Eq. (97*b*) is substituted in this, Eq. (301*d*) is obtained directly. It is to be observed that this derivation of the radiation law does not make use of the Einstein frequency law, which is fundamental for all emission processes. The reason for this is that for the Planck oscillator the frequency μ of the oscillator, at least for energy transitions into neighboring states, coincides with the frequency ν of the emitted wave. (For a Planck oscillator with the frequency μ we have $U_1 = n_1h\mu$; $U_2 = (n_1 - 1)h\mu$; by applying the frequency law we get $\nu = \mu$.)

For the intensity E_λ of the radiation it is found from Eqs. (301*d*) and (297) that

$$E\lambda = \frac{V_l{}^2 h}{\lambda^5} \cdot \frac{1}{e^{\frac{V_l h}{k\lambda T}} - 1}. \qquad (301e)$$

A comparison of this equation with Eq. (298) leads to the relations $c_1 = V_l{}^2 h$, $c_2 = \frac{V_l h}{k}$, from which both of the universal constants h and k or $\mathbf{N} = \frac{R}{k}$ may be calculated from the values of c_1 and c_2 given by radiation measurements. From the above given quantities we get

$$h = 6.55 \cdot 10^{-27}$$
$$k = 1.373 \cdot 10^{-16}$$
$$\mathbf{N} = 6.05 \cdot 10^{23}.$$

4. THE LINKAGE OF ATOMS

a. CHEMICAL VALENCE

345. Heteropolar and Homopolar Compounds.[1]—The basis of the following considerations is the assumption that a chemical union of two atoms is effected by means of the electrons of the outer group; these electrons are often referred to as the **valence electrons.** A chemical combination occurs whenever one or more of the valency electrons belonging originally to one atom enter simultaneously into the assemblage of another atom. Two limiting cases are to be distinguished which lead to the classification of chemical compounds into two groups.

1. The valence electron is *almost completely* removed from the one atom and enters the assemblage of the other; the first atom thus becomes a positively charged ion, and the second a negative ion. Such compounds, which are said to be **heteropolar** and which decompose with relative ease into ions, are held together mainly by Coulombian electrostatic forces.

2. In the other case, the valence electrons describe such orbits (in the compound) that they belong equally to both atoms; since these atoms have the same electric charge, such compounds

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[1] * Often called *polar* and *non-polar* compounds.

are called **homopolar.** They show no tendency to dissociate into ions.

A large portion of the chemical compounds can be classified in these two limiting groups without much difficulty. Of course, rigorously homopolar compounds exist only in the union between two atoms of the same species, such as is found in H_2, O_2, N_2, etc. As soon as different kinds of atoms combine, some dissymmetry in the division of the electric charge can always be observed by such means as the existence of an infra-red spectrum. In a large number of compounds, especially those in which carbon takes part, this dissymmetry is relatively trifling, so that without doubt they can be classified as homopolar compounds in agreement with their other properties.

It may be remarked that in earlier times the contrast between the heteropolar and homopolar compounds led to two fundamentally different conceptions of the nature of chemical valence, which as the dualistic theory (led by Berzelius) and the unitary theory (led by Dumas) sometimes occasioned great dispute. According to the modern conceptions, both ideas are equally correct, but neither of them embraces all compounds

346. Abegg's Law of the Sum of the Maximum Valencies.—If the heteropolar compounds are first considered, it will be seen that they were correctly interpreted even in rather early times. Berzelius in particular made a sharp distinction between electropositive and electronegative valences; in the former, valence electrons were given up, while in the latter one or more additional electrons were taken on. In polyvalent compounds the number of valence electrons transferred is equal to the valence. Correspondingly, an element which had the ability to lose n_e valence electrons is said to be an n_e-valent positive element, one that can add n_e valence electrons is an n_e-valent negative element. A number of elements have different valences in their various compounds; frequently an element which is positive in one compound is negative in another.

Abegg in 1906 emphasized the fact that the sum of the maximum positive valence and the maximum negative valence of an element is always equal to 8. Nitrogen may be taken as an example, as it has a maximum negative valence of 3 in NH_3, and a maximum positive valence of 5 in N_2O_5; chlorine and the other halogens have their maximum negative valency of 1 in HCl, and a maximum positive valency of 7 in Cl_2O_7. In a compound, a halogen can take on one additional electron or lose a maximum of seven.

b. CHEMICAL VALENCE AND ATOMIC STRUCTURE

347. The Formation of the Stable Electron Groups in the Atoms of the Noble Gases.—Since the noble gases, as far as is known at present, are unable to enter into compounds which are stable to any degree,[1] it must be assumed that the electron arrangements in these atoms under normal conditions are particularly stable.

Following the elements in the order of their atomic numbers, it is evident that the electron added at each step in the series cannot be held with equal strength, but that certain very closely correlated electron groups must be formed, a result which has already been indicated by consideration of the internal spectra. At each noble gas one of these groups is completed. However, only the first two groups (the K- and L-groups) are definitely completed in the noble gas structure; the higher groups subsequently undergo a further increase in their electron number beyond the number attained by the noble gas (see **348**).

Only those electrons which are located outside of the group closed by the noble-gas configuration are to be considered as valence electrons. This explains why in the periodic system elements are found at the same distance from a noble gas, which are chemically similar, and why the positive valence increases from left to right while the negative valence increases in the opposite direction. The elements involved possess the same number of valence electrons; in proceeding from left to right this number increases by one unit at each step.

According to Kossel[2] all atoms tend to attain the electron configuration of the noble gases, because these configurations are the most stable; therefore, all atoms attempt, as far as the possibility for doing so exists, either to give up all the valence electrons (electropositive valence), so that each arrives at the electron number of the preceding noble gas, or to take on so many electrons that the outer electron group will be brought up to the number of electrons of the next higher noble gas. By this means Abegg's rule, according to which the sum of positive and negative valences is equal to 8, can be simply explained for at least the lighter atoms up to Ca; up to this point the difference between two successive noble gases is actually eight electrons. For the heavier atoms the relations are somewhat more complex, due to the appearance of another phenomenon (see **348**).

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[1] In spectral tubes in which the atoms are strongly excited because of the influence of the electrical discharge, the labile compound He_2 forms, as is indicated by the appearance of a band spectrum. The existence of this compound is easily understood from the considerations in **330** (see LENZ, W., *Verh. Deut. physik Gesell.*, **21**, 637 (1919)).

[2] *Ann. Physik.*, **49**, 229 (1916). Also *LEWIS, G. N., *J. Am. Chem. Soc.*, **38**, 762 (1916).

The reason why even configurations with quite definite numbers of electrons are particularly stable cannot be explained theoretically at present on the basis of a complete theory. From a purely mechanical standpoint a particularly stable state of a system is the result of a pronounced minimum in its energy content. Actually, for example, when a four-quantum orbit is added to argon with one more nuclear charge (the formation of the potassium atom), the energy of a 4_1-orbit is considerably less, *i.e.*, the negative energy is greater, than that of a 4_2-, 4_3-, or 4_4-orbit (see **328**). However, the quantum conditions play a decisive rôle in determining the electron configurations in the atom. For example, it frequently happens that the configuration which is the most stable mechanical group cannot be realized on account of some *quantum restriction*. It seems that the exact conditions favorable to an attainable, stable configuration are always fulfilled when the structure involved possesses a high degree of symmetry. Therefore it has been attempted to bring the arrangement of electrons in a group of eight into relation with the distinctive symmetrical properties of the cube and to find an explanation for its great stability in this fashion.[1]

348. The Arrangement of Electrons in Chemical Elements.—By means of the recent investigations by N. Bohr it has become possible essentially to complete the general picture of the whole atom previously obtained in which the atom consists of a number of sharply separated electron groups. The advance consists mainly in the fact that Bohr has been able to draw certain conclusions regarding the nature of the orbits of the individual electrons from a number of properties (predominantly optical). Bohr considered the atoms of the entire periodic system as built up by increasing the nuclear charge in steps of one unit each, and at the same time adding on an electron from the outside. As shown in **328**, the type of the orbit of the new electron can then be determined in a number of cases.[1]

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[1] See LANDÉ, A., *Verh. Deut. physik Gesell.*, **21**, 2, 644, 653 (1919); *Z. Physik.*, **2**, 83 (1920); * further, a number of articles, by G. N. Lewis and by I. Langmuir (see footnotes to **347** and **349**). An excellent summary of the theories of "cubic atoms" is given in the monograph on "Valence and the Structure of Atoms" (Chemical Catalog Co. (1923)) by G. N. Lewis.

We now have as a fundamental law that an electron previously added generally retains its type of orbit, i.e., its quantum numbers, even when heavier atoms are formed by further increasing the nuclear charge and adding on new electrons. Of course, the dimensions of the orbits already present will not be retained; as a result of the increase of the nuclear charge they must decrease more and more as the atom becomes heavier.

The entire result of Bohr's investigation is contained in Table 77.

The innermost (K-) group is completed at helium, *i.e.*, a newly added electron can no longer find place in the K-group, which consists of two crossed, one-quantum, circular orbits (see **330**), and it is therefore compelled to describe a two-quantum orbit.

Thus the formation of the second (L-) group begins with lithium ($Z = 3$). The question whether the added electron occupies a 2_1-orbit or a 2_2-orbit is decided absolutely in favor of the 2_1-orbit by the behavior of the external spectrum. The considerations which were employed in **328** for the orbit of the outer electron of potassium remain essentially the same for lithium also, but, on account of the relatively weak nuclear charge, the electron does not penetrate the K-group but merely approaches very close to it from the outside. For beryllium the addition of one more 2_1-orbit is to be assumed, while in boron it is uncertain whether the new electron describes a circular or an

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[1] In these investigations by Bohr the conclusions which are to be drawn directly from the experiments are more prominent than purely theoretical calculations.

TABLE 77.—NUMBER OF DIFFERENT ELECTRONIC-ORBIT TYPES IN ELEMENTS IN THE NORMAL STATE (*Bohr*)

Group		*K*	*L*		*M*			*N*				*O*					*P*						*Q*	
Z	$n_{n'}$	1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	5_4	5_5	6_1	6_2	6_3	6_4	6_5	6_6	7_1	7_2
1	H	1																						
2	He	2																						
3	Li	2	1																					
4	Be	2	2																					
5	B	2	2	(1)																				
10	Ne	2	4	4																				
11	Na	2	4	4	1																			
12	Mg	2	4	4	2																			
13	Al	2	4	4	2	1																		
18	Ar	2	4	4	4	4																		
19	K	2	4	4	4	4		1																
20	Ca	2	4	4	4	4		2																
21	Sc	2	4	4	4	4	1	2																
22	Ti	2	4	4	4	4	2	2																
29	Cu	2	4	4	6	6	6	1																
30	Zn	2	4	4	6	6	6	2																
31	Ga	2	4	4	6	6	6	2	1															
36	Kr	2	4	4	6	6	6	4	4															
37	Rb	2	4	4	6	6	6	4	4			1												
38	Sr	2	4	4	6	6	6	4	4			2												
39	Y	2	4	4	6	6	6	4	4	1		2												
40	Zr	2	4	4	6	6	6	4	4	2		2												
47	Ag	2	4	4	6	6	6	6	6	6		1												
48	Cd	2	4	4	6	6	6	6	6	6		2												
49	In	2	4	4	6	6	6	6	6	6		2	1											
54	X	2	4	4	6	6	6	6	6	6		4	4											
55	Cs	2	4	4	6	6	6	6	6	6		4	4				1							
56	Ba	2	4	4	6	6	6	6	6	6		4	4				2							
57	La	2	4	4	6	6	6	6	6	6		4	4	1			2							
58	Ce	2	4	4	6	6	6	6	6	6	1	4	4	1			2							
59	Pr	2	4	4	6	6	6	6	6	6	2	4	4	1			2							
71	Lu	2	4	4	6	6	6	8	8	8	8	4	4	1			2							
72	Hf	2	4	4	6	6	6	8	8	8	8	4	4	2			2							
79	Au	2	4	4	6	6	6	8	8	8	8	6	6	6			1							
80	Hg	2	4	4	6	6	6	8	8	8	8	6	6	6			2							
81	Tl	2	4	4	6	6	6	8	8	8	8	6	6	6			2	1						
86	Em	2	4	4	6	6	6	8	8	8	8	6	6	6			4	4						
87	—	2	4	4	6	6	6	8	8	8	8	6	6	6			4	4					1	
88	Ra	2	4	4	6	6	6	8	8	8	8	6	6	6			4	4					2	
89	Ac	2	4	4	6	6	6	8	8	8	8	6	6	6			4	4	1				2	
90	Th	2	4	4	6	6	6	8	8	8	8	6	6	6			4	4	2				2	

elliptical orbit. If, from reasons of symmetry, four 2_1-orbits are assigned to the next element, carbon, as seems to be quite appropriate, then in boron also only 2_1-orbits could be present, provided the principle of invariability of quantum numbers always holds. However, since this principle certainly breaks down in several cases (such as Cu), it is probable that it also happens in the transition from boron to carbon.

When another electron is added in the formation of nitrogen, the symmetry would be very much disturbed if it likewise described a 2_1-orbit; the only possibility remaining is a circular 2_2-orbit. The succeeding atoms are also formed by adding on more 2_2-orbits until at neon the L-group with four 2_1-orbits and four 2_2-orbits is completed

The building up of the third series (M-group) of the periodic system (Na to A) takes place in exactly the same way as in the second series; first the electron enters in the form of 3_1-orbits, later in the form of 3_2-orbits. In these cases, however, the interpretation of the spectroscopic data is altogether in favor of a 3_2-orbit for the added electron in Al, and not a 3_1-orbit (the largest term corresponding to the most stable orbit is not in this case, as it is in the alkali and alkaline earth metals, an *s*-term but a *p*-term (see **328**)). It is noteworthy that, compared to the building up of the second series, the end of the series at A, a number of possible orbits (the 3-orbits) belonging to the M-group have not yet appeared.

However, in the formation of the fourth series this gap becomes filled. At first, of course, just as in the earlier groups, two 4_1-orbits are occupied (K and Ca); but at scandium the unfinished M-group begins to be completed by the appearance of a 3_3-orbit. The fact that, from element 21 (Sc) on, the M-group must be completed has already been disclosed in **324** by the behavior of the internal spectrum.

One of the reasons why beyond a certain point the 3_3-orbit, which in potassium is still rather far removed from the nucleus, is more stable in scandium than a 4_1-orbit is without doubt to be found in the fact that, upon increasing the true nuclear charge by two units, the effective nuclear charge of the whole 3_3-orbit (which lies outside of the kernel) is multiplied by 3; the diameter of the 3_3-orbit must, therefore, decrease by one-third, while in the 4_1-orbit only the force acting on the outer portion of the orbit is trebled. Therefore, on the average, in the transition from K to Sc the negative value of the energy and the stability of 3_3-orbit increase more than those of the 4_1-orbit. Further, a comparison of the arc spectrum of K and Ca shows that even in Ca the difference between the energy of the 3_3-orbit (the first *d*-term) and that of the 4_1-orbit (first *s*-term) is much less than in K.

In the next following elements also (Ti, V, etc.), the new electrons enter into the M-group; after a certain point, which has not yet been definitely established, even the number of 3_1- and 3_2-orbits is increased from 4 to 6. This enlargement of the M-group is finally concluded at element 29 (Cu); from this point on the added electrons again place themselves in 4_1- and 4_2-orbits in the normal fashion.

The discovery that between Sc and Cu the electrons do not simply take up outside positions agrees very well with the chemical behavior of these elements.[1] Here for the first time there is met a series of elements with metallic characters, each of which has several different positive valences; if the compounds of neighboring elements at the same valence level are compared, a certain similarity in their physical and chemical properties is found which otherwise occurs only within the vertical series of the periodic system.

The variation in the valence of these elements is explainable because the added 3_3-electrons in the M-group are, at least to some extent, quite as easily removed from the atom as the 4_1-electrons already present. The significance of the similarity in the chemical compounds of the neighboring elements at the same valence level is to be found in that, after a definite number of electrons has been separated, the remaining part of the atom is not so very different from one element to the next.

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[1] It should be noted that all the elements in which the added electron takes an inside position are distinguished by the *following physical properties*: *small atomic volumes*, *paramagnetism in their compounds* (the compounds of all other elements are diamagnetic), *colored ions in aqueous solution* (see Fig. 57). The smallness of the atomic volume can be explained directly by the fundamental assumptions; a theoretical explanation of the other two properties, in so far as this would be possible at the present time, lies beyond the scope of this book.

The final completion of the M-group after reaching its full number of electrons is by no means so definitely marked as the earlier completion of the 3_1- and 3_2-orbits at argon; yet it follows from the chemical behavior that the electrons of the M-group, as the group approaches completion, are held considerably more firmly than previously. While at Mn five electrons are easily removed from the M-group, in the elements from Fe to Cu only one electron of this group is able to participate in chemical reactions. An exception occurs in the case of Cu, where even one of the 4_1-orbits of the previous element is changed to a 3_3-orbit, this showing with particular clearness the tendency of the M-shell to complete its configuration. That Cu actually has only *one* outer 4_1-orbit follows without any doubt from the great similarity between the arc spectra of Cu and the alkali metals.

The formation of the fifth (O-) group of the periodic system takes place in exactly the same way as that of the third and fourth groups, only now there are 5_1- and 5_2-orbits instead of the 4_1- and 4_2-orbits of the N-groups, and the 4_3-orbit instead of the 3_3. It is to be observed that at first no 4_4-orbits develop, and therefore a gap remains open, as in the formation of the third group.

The sixth group (P-group), analogous to the others, begins with the addition of two 6_1-orbits to the xenon configuration (the formation of Cs and Ba); the next electron, likewise quite analogous to the previous cases, enters a 5_2-orbit in the O-group. Now, however, a new process begins with the formation of the **rare-earth elements.** *The next fourteen electrons do not enter the O-group but the still deeper N-group;* they first fill up the empty 4_4-orbits, but, besides this, increase the 4_1-, 4_2-, 4_3-orbits already present from six to eight electrons.

These facts, which are important for the understanding of the entire periodic system, follow directly from the relations between the internal sepctra, and were discussed in **324.**

It is due to the relatively deep-lying position taken up by the added electron that the outward effect[1] of the kernel in this part of the periodic system changes very little from element to element; in this way the great similarity of the physical and chemical properties of the rare earths and their compounds are easily explained.

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[1] The effect of an electron orbit towards the outside of the atom obviously depends less upon its mean than upon its maximum distance from the nucleus. Thus, a new circular 4_4-orbit has much less effect on the external atomic properties than an elongated 6_1-orbit, even when the mean nuclear distances of the two are not far different.

Only when element 72 (hafnium), which has just recently been discovered, has been reached is it possible to continue building up the 5_3-orbits of the O-group, which began at lanthanum. Thus we get an atom whose external structure corresponds to that of zirconium, and therefore, according to Bohr, it must be a chemical homologue of this element, although it had previously been considered as belonging to the rare earths.[1] In this way the path to its discovery was indicated; actually, it has been discovered in zirconium minerals by Coster and v. Hevesy.[2]

Of the seventh group only five elements are known; the placement of the added electrons without doubt occurs in the same way as in the previous groups. At elements 87 (not yet discovered, probably a strongly radioactive alkali metal) and 88 (Ra) we find 7_1-orbits for the first time, and at actinium 6_3-orbits. For the completion of the missing 5_3- and 5_4-orbits which would be expected in analogy with the behavior of the O-group, it is remarkable that no indication exists.[3]

c. THE STRUCTURE OF MOLECULES

α Heteropolar Compounds

349. Models of Heteropolar Compounds.—According to **341** a heteropolar molecule arises from the transfer of valence electrons from one atom to another, *i e.*, from the electropositive to an electronegative atom. As an example, the compound HCl may be considered to be formed from one chlorine and one hydrogen atom. At the beginning, the inner part of the chlorine atom is surrounded by seven outer electrons. Since the ten electrons near the nucleus are not involved in the formation of molecules, the neutral chlorine atom behaves as a kernel with seven charges surrounded by seven outer (valence) electrons. If the valence electron of hydrogen is added to these, it might be assumed that the electrons are arranged on the corners of a cube while the hydrogen nucleus is fixed outside of the cube somewhat as indicated in Fig. 89. As a result of the mutual repulsion of the nuclei and the attraction of the nuclei by the electrons, the cube of electrons is displaced slightly towards the hydrogen nucleus. *It is clear that the model cannot be an accurate representation of the actual structure, since it considers neither the movements nor the centrifugal forces of the electrons to which the structure as a whole owes its stability.* Although in the model shown in Fig. 89 the centrifugal force is replaced by an unknown force which holds the electrons rigidly on the corners of the cube, yet it seems as if this model correctly reproduces many of the properties of hydrogen chloride.

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[1] * Bury (*J. Am Chem. Soc*, **43,** 1602 (1921)) by a modification of the Lewis-Langmuir theory secured the same numbers of electrons in the various shells as Bohr. He also predicted that element 72 should resemble Zr. These two investigators arrived at these conclusions by means of such totally different considerations that no question of priority is involved

[2] *Naturwissenschaften*, **11,** 133 (1923),* and *Chemical Reviews*, **2,** 1, (1925)

[3] Even before Bohr had developed his detailed theory of the periodic system, R Ladenburg (*Naturwissenschaften*, **8,** 6 (1920); *Z Elektrochem*, **26,** 262 (1920)) showed that, contrary to the conception prevailing at that time, in progressing along the periodic system the added electron did not appear to take up a place in the outer portion of the atom in a number of elements, but that it went deeper into the structure. The conception developed by him that this took place by the formation of special "intermediate shells" is unnecessary now.

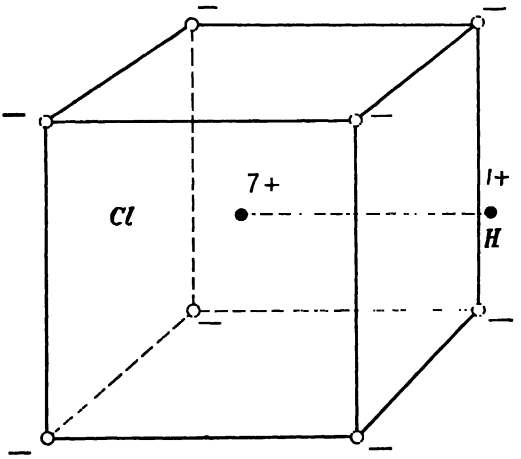

Fig. 89

In analogy with this molecule, the models of the other heteropolar compounds have also been represented by cubes; as a first approximation the sodium chloride molecule would be represented by two nearly rigid cubes lying side by side.[1]

In a number of cases it is possible to use still simpler models. Suppose that all the atoms of a heteropolar compound are completely ionized and regard the ions simply as approximately rigid spheres[2] which according to their charges either repel or attract each other. The coherence of a heteropolar compound is then determined only by Coulomb's law, and we have for the work A' of decomposing a simple molecule consisting of two oppositely charged ions, the expression

$$A' = \frac{e_1e_2}{r_1 + r_2}, \tag{302}$$

where r_1 and r_2 are the radii of the two ionic spheres.

350. Calculation of the Affinity of Formation of a Heteropolar Compound.—The formation of a heteropolar compound from two neutral atoms, which were originally at an infinite distance from each other, can be considered to take place in such a manner that the valence electron is transferred from the electropositive atom to the electronegative, or, what amounts to the same thing, first take the electron away from the electropositive atom and then give it to the electronegative; during the process both atoms become ionized. The formation of the compound thus occurs in such a way that, due to their electrostatic charges, the ionic spheres approach each other as closely as their radii permit.

The **affinity of formation** or the **heat of formation** A of a simple binary gaseous compound from its ions thus consists of the negative work of ionization J_1 and J_2 of the two atoms, together with the electrostatic work A' which will be performed by the approach of the spherical ions to the distance $r_1 + r_2$.

$$A = -J_1 - J_2 + A'.$$

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[1] * See LANGMUIR, *J. Am. Chem Soc.*, **41**, 868 (1919). A simpler exposition of the theory is given by Elwood Hendrick (*Chem Met. Eng*, **21**, 73 (1919)). Langmuir discusses the application of the theory to nitrogen compounds and complete ionization of salts in *J. Am. Chem. Soc*, **42**, 274 (1920).

[2] By means of the rigidity of the spheres the mutual repulsion of the outer electrons is brought into the calculation.

For the formation of HCl the following data exist: the work of ionization of hydrogen according to **310** is simply equal to $h\nu_\infty$, where ν_∞ is the limiting frequency of the Lyman series, or also $\mathfrak{R}V_l h$ (per atom), or $\mathfrak{R}V_l h\mathbf{N} = 1.3 \cdot 10^{13}$ *ergs* = 310,000 *cal.* (per mole). The work of ionization for the chlorine atom can only be found indirectly and amounts to approximately −90,000 *cal.* per mole, *i.e.*, the Cl atom has the tendency to ionize spontaneously, while the ionization of the H atom requires work to be performed on it from an outside source. The work of separating HCl into ions[1] if the distance $r_1 + r_2$ be set at $1 \cdot 10^{-8}$ in round numbers amounts to $A' = 330{,}000$ *cal.* However, greater accuracy may be claimed for the value 315,000 *cal.* determined directly from the ionization potential by P. Knipping.[2] It follows, then, that the affinity of formation of the molecule from the atoms is

$$A = -310{,}000 + 90{,}000 + 315{,}000 = \text{about } 95{,}000 \ cal.$$

In order to compare this value with the observed heat of formation, 22,000 *cal.* of HCl from elementary (diatomic) chlorine and hydrogen, the work or heat of dissociation of the two elements into atoms must be taken into consideration. For chlorine this amounts to about 30,000 *cal.* per gram atom, for hydrogen to about 45,000 *cal.* The observed heat of formation of HCl from the atoms is, thus, 22,000 + 30,000 + 45,000 = 97,000 *cal.* The agreement between this value and the one calculated above may be considered as quite satisfactory in view of the uncertainty of some of the data involved in the calculation.

It is thus seen that in the gaseous state the dissociation of HCl into atoms takes place much more readily than the dissociation into ions, since the work of dissociation, A = about 100,000 *cal.*, is considerably less than the work of ionization, $A' = 315{,}000$ *cal.*

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[1] Due to the displacement of the atomic nuclei towards one side (**349**), the distance between the midpoints of ionic spheres, which is involved in this calculation, is in any case less than the distance $1.28 \cdot 10^{-8}$ determined from the atomic nuclei given in Table 76.

[2] The value given by P. Knipping (*Physik. Zeit.*, **7**, 328 (1921)) for the ionization potential of HCl has been corrected by J. Franck, (*ibid.*, 160 (1922)).

351. Electrolytic Dissociation of Heteropolar Compounds in Aqueous Solution.—The relations in aqueous solutions are quite different, as experience shows, in that the molecules are practically completely ionized and therefore the work of separating the compound into its ions must be very much less.

In formal terms, an explanation for the reduction of the work of ionization A' is obtained when it is noted that the effective force between two electric charges is inversely proportional to the dielectric constant D of the medium between them. Since for water $D = 80$, the work of ionization is $\frac{315{,}000}{80} \simeq 4000$ *cal.*, which is so small that even at room temperature an extensive separation of the ions seems to be quite likely as the result of the heat motion of the atoms. That this consideration can represent only a rough approximation may be seen from the fact that *the main part of the work is performed in separating the ions to molecular distances, by which the conception of the dielectric constant, which holds for a continuum, loses its meaning.*

If we do not wish to treat the influence of the solvent in a too arbitrary fashion and yet desire to avoid the use of the dielectric constant, then we may try to determine in what manner an isolated, *gaseous* ion would enter into a reaction with the solvent. In various ways it can be shown that, by the addition of detached ions to the molecules of the solvent (especially in water), a very considerable electrical work of "hydration" A_h is set free, which is about as large as or, in many cases, is even larger than the work of separating the ions A'. In the case of HCl, it is found from various considerations (see **352**) that the approximate value of the work of hydration is about 250,000 *cal.* for the H ion and about 100,000 *cal.* for the Cl ion, so that the total work of hydration for the detached ions is about 350,000 *cal.*, which is somewhat larger than the work A'. Therefore in the solvent the ions will not combine with each other to form neutral molecules, but will unite individually with molecules of the solvent to form "hydrates" and thus remain separated from each other.

352. The Influence of the Charge and Size of the Ionic Sphere on the Chemical and Electrochemical Behavior of the Heteropolar Compounds.—If the exchange of the valency electrons is considered as being completed and the heteropolar compound is thought of as simply being built up of ionic spheres, then, as Kossel has shown, a number of chemical properties of heteropolar compounds can be most simply understood by means of a purely electrostatic explanation in place of the more complicated chemical explanation which had been previously sought.

As the characteristic properties of ions which are significant in the formation of heteropolar compounds it is only necessary to consider:

1. The magnitude of the charge.
2. The radii of the ionic spheres.

As Kossel was able to show, the size of the charge exercises a decisive influence on the entire behavior of heteropolar compounds.

A simple example may be found by comparing the three hydrogen compounds HCl, H_2O, and NH_3, in which the charge of the anions increases from 1 (Cl) to 3 (N) As a result of this increasing charge, the hydrogen ion is relatively loosely bound in HCl, considerably more strongly in H_2O, but in NH_3 it is so firmly held than no measurable amount of H^+ ion dissociates off.

The triple negative charge of the nitrogen permits not only a very firm binding of the H ions originally present, but also acts powerfully upon other ions which do not yet belong to the molecule, so that monovalent positive ions can be superimposed upon the nitrogen in addition to the three hydrogens. If, for example, a neutral NH_3 molecule is brought into contact with an H^+ ion, the ion NH_4^+ is formed. Of course, the similarly charged H^+ ions, repel each other, which counterbalances the attraction of the nitrogen, but the repulsion of four monovalent ions is still smaller than the attraction.

On the basis of the above assumption it may be calculated numerically how many monovalent ions can be added on an m-valent ion. If there be no motion of the molecules due to heat, that combination will always be formed for which the potential electrostatic energy is a minimum or for which, by the union of the constituents, the electrical work performed is a maximum. At higher temperature, of course, the most stable compounds again decompose partially, due to the heat motion of the molecules. The electrostatic work is composed of the work of attraction

$\Phi_m = \frac{n''me^2}{r_1 + r_2}$ of the inner m-valent ionic sphere (radius r_1) on the n'' other ions (radius r_2), each of which carries an opposing *single* charge, as well as the work of repulsion Φ_r of the latter upon each other.

For Φ_r the following values are obtained for an increasing number n'' of the ions whose centers, as a result of their repulsive actions, are arranged on a sphere of radius $r_1 + r_2$ in the most symmetrical, regular manner possible:

$$n'' = 2 \ : \ \Phi_r = \frac{1}{2}\frac{e^2}{r_1 + r_2}; \quad n'' = 3 \ : \ \Phi_r = \frac{3}{\sqrt{3}}\frac{e^2}{r_1 + r_2} = 1.73\frac{e^2}{r_1 + r_2};$$

$$n'' = 4 (tetrahedra): \ \Phi_r = \frac{6\sqrt{6}}{4}\frac{e^2}{r_1 + r_2} = 3.676\frac{e^2}{r_1 + r_2};$$

$$n'' = 5 \ : \ \Phi_r = \left(\frac{3}{\sqrt{3}} + \frac{6\sqrt{2}}{2} + \frac{1}{2}\right)\frac{e^2}{r_1 + r_2} = 6.48\frac{e^2}{r_1 + r_2};$$

$$n'' = 6 (octahedra) \ : \ \Phi_r = \left(\frac{12\sqrt{2}}{2} + \frac{3}{2}\right)\frac{e^2}{r_1 + r_2} = \frac{10e^2}{r_1 + r_2}, \text{etc.}$$

Considering a trivalent nitrogen ion ($m = 3$) to which single-charge H^+ ions are brought from an infinite distance, the factors by which the quotient $\frac{e^2}{r_1 + r_2}$ of the total work performed $\Phi_m - \Phi_r$ are to be multiplied form a series of values as follows: for $n'' = 2$, 5.50; $n'' = 3$, 7.27; $n'' = 4$, 8.32; $n'' = 5$, 8.52; $n'' = 6$, 8.00. Since the maximum lies at $n'' = 5$, an ion NH_5^{++} should be formed in a solution containing free H^+ ions, but the work of separation of the fifth H^+ ions is so small that even at room temperature it is practically completely dissociated and only the NH_4^+ remains.

In a pure aqueous solution of NH_3, in which the concentration of H^+ ions is very slight from the beginning, it is well known that for a portion of molecules an H^+ ion leaves the compound H_2O and attaches itself to the NH_3, so that in the solution NH_4^+ ions and OH^- ions are present.

This case may also be easily calculated. The electrostatic energy $\Phi_m - \Phi_r$ of the H_2O and NH_3 molecules amounts, respectively, to $3.50 \frac{e^2}{r_1 + r_2}$ and $7.27 \frac{e^2}{r_1 + r_2}$, and together to $\frac{10.77e^2}{r_1 + r_2}$, if the same diameters are assigned to the $O^{=}$ and N^{+++} ions. On the other hand, the electrostatic energy of the OH^- and NH_4^+ ions amounts to

$$\Phi_m - \Phi_r = (2.00 + 8.32)\frac{e^2}{r_1 + r_2} = 10.32 \frac{e^2}{r_1 + r_2}.$$

It is thus shown that the affinity of formation of the neutral molecules from the individual ions is the greater, yet the energy difference between the two systems, $NH_3 + H_2O$ on the one side and $NH_4^+ + OH^-$ on the other, is rather small, so that it is not difficult to understand that, as a result of the heat motion of the molecules, a portion of them are found in the ionized states NH_4^+ and OH^-. These considerations lead to the further result that the undissociated hypothetical compound NH_4OH cannot form at all or at the most in exceedingly small amounts, since the repulsion between the doubly charged negative O ion and the trebly charged negative N ion is much too great.

An example which is completely analogous to the formation of the NH_4^+ ion, but which involves a triple positive charge on which are added monovalent negative ions, is found in the molecule $AuCl_3$, which unites with a Cl^- ion to form the $AuCl_4^-$ in an HCl solution.

For an ion with four charges like the Pt^{++++} ion the possibility of adding on oppositely charged, simple ions is considerably greater than for an ion with three charges. The calculation shows that the electrostatic work $\Phi_m - \Phi_r$ involved in the union of ions is a maximum for six added monovalent ions, which agrees with the chemical result that a $PtCl_6^{=}$ ion is formed in HCl solution. If to such a solution NH_3 molecules are added, it is possible, on account of the triple charge of the nitrogen, to displace the Cl^- ions wholly or in part, so that there are formed radicals or ions such as $Pt(NH_3)Cl_5^-$, $Pt(NH_3)_2Cl_4$, $Pt(NH_3)_3Cl_3^+$, $Pt(NH_3)_4Cl_2^{++}$, $Pt(NH_3)_5Cl^{+++}$, $Pt(NH_3)_6^{++++}$. A greater electrostatic work is performed in the formation of the system $Pt(NH_3)_6^{++++} + 2H^+ + 6Cl^-$ from the individual ions Pt^{++++}, N^{---}, etc. than in the formation of the system $PtCl_6^{--} + 2H^+ + 6NH_3$.

In a similar manner it is possible to explain, from a purely electrostatic viewpoint, a number of other phenomena in the field of the inorganic complex compounds, especially the so-called "molecular compounds," the understanding of which involves certain difficulties from the older chemical viewpoint, and which required the existence of "coordinative linkage," as distinguished from the ordinary chemical valence, to be assumed.

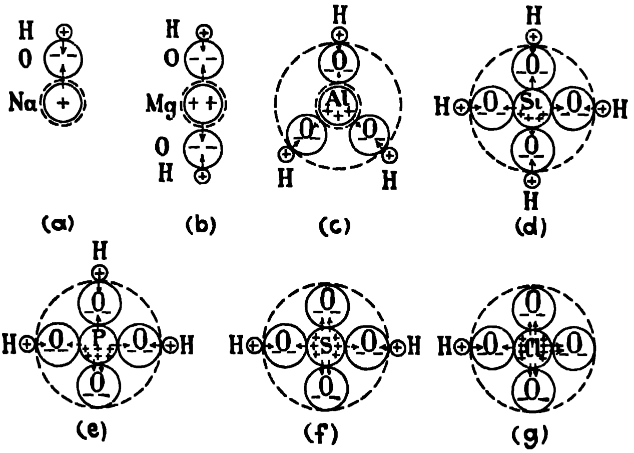
The hydration of ions already mentioned in the preceding paragraph may be explained, at least schematically, by simple electrostatic addition, even though the relations are somewhat different from those in the formation of the NH_4^+ ion, etc., since the individual ions are completely surrounded by the molecules of the solvent and the individual ion is apparently not bound to any definite molecule of the solvent. In spite of this, the sort of calculation illustrated by the above example seems to lead to at least approximately correct results for hydration also. It may thus be assumed that an H^+ ion in water adds on only one H_2O molecule. Since the electrical work involved in the formation of the H_2O molecule from one doubly charged O ion and two H^+ ions is $(2 \times 2 - \frac{1}{2})\frac{e^2}{r_1 + r_2} = 3.5\frac{e^2}{r_1 + r_2}$, but the formation of the complex H_3O^+ involves only $(3 \times 2 - \sqrt{3})\frac{e^2}{r_1 + r_2} = 4.27\frac{e^2}{r_1 + r_2}$, there is found for the hydration $H^+ + H_2O$ the work

$$(4.27 - 3.5)\frac{e^2}{r_1 + r_2} = 0.77\frac{e^2}{r_1 + r_2}.$$

If $r_1 + r_2$ is again put equal to $1.0 \cdot 10^{-8}$, the work of hydration per mole is found to be $A_h \simeq 255{,}000$ *cal.* The Cl^- ion can fasten itself to the H_2O only on the outside of the molecule on one of the H ions: $Cl^- - H^+ - O^{--} - H^+$. Since the attraction between an H^+ ion and the Cl^- ion striking it directly is compensated by the repulsion of the O^{--} ion (doubled distance but doubled charge!), practically only the attraction between the Cl^- ion and the more distant H^+ ion remains. The work corresponding to this attraction as the result of the distance $3(r_1 + r_2)$ amounts to $A_h = \frac{1}{3}\frac{e^2}{r_1 + r_2}$ or, expressed in calories per mole, 100,000 *cal.* Thus altogether, the work of hydrating a mole of H^+ ions and Cl^- ions in the gaseous state is about 350,000 *cal.*, while experimentally the value of about 330,000 *cal.* was obtained. On the basis of Hess' law the heat of hydration of the gaseous ions is equal to the work of ionization of the gaseous molecule (315,000 *cal.*) plus the heat of solution (17,000 *cal.*).

In order to illustrate the influence of the ionic diameters upon the behavior of heteropolar compounds (although in comparison with that of the ionic charge this effect is rather small), the four compounds H_2O, H_2S, H_2Se, and H_2Te may be compared with respect to each other. It must be assumed that the ionic radius increases from O to Te. Therefore, the H^+ ions are held more firmly by the doubly charged negative ion in H_2O than in H_2S, in H_2S more firmly than in H_2Se, etc. This supposition is confirmed by the measured electrolytic dissociation constant (affinity constant) which for H_2O is about 10^{-14}; for H_2S, about $1 \cdot 10^{-7}$; for H_2S, about $1.7 \cdot 10^{-4}$; and for H_2Te, about 10^{-2}.

An instructive example, in which the simultaneous influence of the length of the radius and the charges of the ions of heteropolar compounds appears, is given by the behavior of the elements of a horizontal row of the periodic system with respect to the radical OH^-.



(a) (b) (c) (d) (e) (f) (g)

Fig 90

It is well known that the compound $X(OH)_n$ will dissociate OH^- ions if X is an alkali or alkaline earth metal, and H^+ ions if X is phosphorus, chlorine, etc., that is, the elements found on the left side of the periodic table have basic properties, while those on the right side are acidic.

It may be assumed that the ionic sphere with *m* charges, which corresponds to the element X, possesses approximately the same diameter in the various elements; the diameter of the hydrogen ion, which consists of a mere nucleus, will be considered as being very much smaller.

The simple, positively charged alkali metal (Na) will be attracted by the oxygen, yet, due to its greater diameter, the oxygen dissociates more readily from the sodium than from the H^+ ion, which is very firmly held to the oxygen because of its small radius (Fig. 90); thus, in solution, OH^- ions are easily formed.

A doubly charged atom (alkaline earths) allows two OH^- ions to be added to it in the manner indicated in Fig. 90*b*, but, due to the double charge of the middle ion, there is already a perceptible repulsive effect upon the H^+ ions *i.e.*, the H^+ ions of the OH^- are somewhat loosened, and the basic character is less distinct than in the previous case. The more the charge on the central ion increases the stronger will the $O^{=}$ ion be held, but, on the other hand, the respulsive force on the H^+ ion will simultaneously become greater.

The compounds $Al(OH)_3$, $Si(OH)_4$, $PO(OH)_3$, $SO_2(OH)_2$, $ClO_3(OH)$ have, therefore, increasingly acidic characters; the last two are exceptionally strong acids (*cf.* Figs. 90*c* to *g*, in which the dotted ring indicates the place where dissociation occurs). The quantitative calculation shows that up to the fourth element (Si) it is easier to split off an OH^- ion from the molecule, but above that it is easier to split off an H^+ ion. Already at phosphorus, the force of repulsion on the H^+ ion is so great that the molecule $P(OH)_5$ is no longer formed at all, but the ion $P(OH)_3O_2^{--}$ is first obtained. But since the $O^{=}$ ions mutually repel each other, one of these dissociates off and unites with the far-removed H^+ ions to form H_2O, so that the neutral molecule $PO(OH)_3$ remains. This, however, still has the tendency to repel the H^+ ions and thus acts as an acid.

The greater the charge on an ion the greater is its effect, not only on the free ions with which it comes in contact but also on the ions contained in other heteropolar molecules; thus the latter are frequently split off and the highly charged ion links together with a number of oppositely charged ions into a firm complex. In this effect of a high ionic charge on a heteropolar compound is to be seen the reason why ions which carry a charge of more than three are not formed in solutions, especially aqueous solutions, or are at most capable of existence only in very small amounts. If it were possible to prepare some of the ion S^{++++++} in the free state, so soon as it was brought into contact with water, the O^{--} ions would be strongly attracted, the H^+ ions strongly repelled, and the following exchange would take place

$$S^{++++++} + 4H_2O = SO_4^{--} + 8H^+.$$

On the whole, it may thus be seen that the chemical and electrochemical behavior of numerous inorganic compounds may be explained in a far-reaching manner by attributing to them a decided heteropolar character and correspondingly considering them schematically as built up of a number of ionic spheres between which only electrostatic forces act. It is clear that this somewhat rough method of treatment cannot always lead to completely correct results. This is the case particularly when the heteropolar character of a compound is not very pronounced, *i.e.*, when the exchange of valence electrons is not complete.

Fajans has performed an investigation to take this into account through the consideration of a "deformation of electron shells" (*Naturwissenschaften*, **11**, 165 (1923)). Although this author arrived at several remarkable qualitative results, it must be considered as doubtful whether permanent advance is produced in this way, because a general applicability of the simple ionic sphere model breaks down rather less on account of the lack of the rigidity which it was necessary to assume at first, than because of the fact that frequently there are actually no completely detached ionic spheres present but, instead, the valence electrons are, at least to some extent, shared between the two kernels

β Homopolar Compounds

353. The Model of the Hydrogen Molecule.—The simplest homopolar compound is the hydrogen molecule H_2. According to an old theory by Bohr, the union of the two atoms is effected by a (one-quantum) ring formed by two revolving electrons, so that the model illustrated in Fig. 91 is obtained. This system is in itself completely stable; the electrons will be attracted

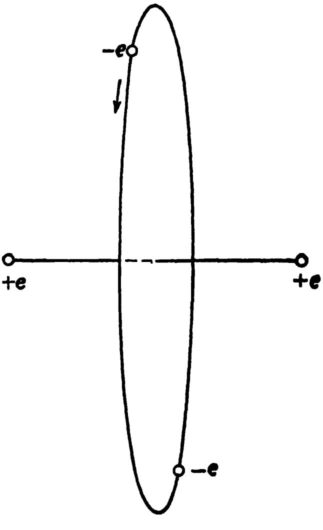


Fig 91.

by the nuclei, but the centrifugal force prevents them from combining. The nuclei are located in stable positions where their mutual repulsions, and the attraction components of the electrons which act in the direction of the lines connecting them, hold the entire system in equilibrium.[1] The shape and the absolute size of the system are then completely determined by the condition that the orbital energy of the electrons must be equal to $\frac{1}{2}h\mu$. Its other physical properties are also absolutely fixed by this condition (*e.g.*, optical properties).

Tests as to whether and in how far the Bohr H_2 model correctly reproduced the observed physical and chemical properties have in several cases (dispersion and magnetic rotation) led to a confirmation of it; in other cases values of at least the correct order of magnitude were obtained, *e.g.*, according to the model the work of dissociation should be about 62,000 *cal* per mole, while the results of measurements by various methods give about 90,000 *cal.*[2] While for a long time, due to this and several other disagreements between experiment and theory, it seemed necessary to abandon Bohr's model altogether, Kramers' discoveries about the helium atom (see **321**) at least open up the possibility that the reason for the disagreement is not to be sought in the incorrectness of the model but rather in the present lack of knowledge concerning the laws which govern the mutual effects of rapidly moving electrons.

Of course, whether it is possible to have a one-quantum ring with two electrons, as Bohr's model assumes, seems to be doubtful from the behavior of orthohelium, whose real 1_1-orbit, which likewise must consist of such an electron ring, actually cannot be realized Just due to this circumstance of the helium atom whose orbits in the normal state cross, a certain probability was given to the supposition expressed by Born (*Naturwissenschaften*, **10**, 677 (1922)) that the orbits of the valence electrons of the hydrogen molecule revolve in planes beyond the line connecting the two nuclei and cutting each other at an angle of 60°. However, L Nordheim showed that such a model was not stable (*Z. Physik.*, **19**, 69 (1923)).

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[1] * However, the model is dynamically unstable, for if one electron is pushed slightly ahead, it will move still farther out of its orbit and the model changes a finite amount from that suggested by Bohr.

[2] * For a recent calculation of the heat of dissociation of H_2, see GRAHAM EDGAR (*J Am Chem Soc*, **45**, 673 (1923)). The values obtained are somewhat less than 90,000 *cal.*, depending upon the temperature.

Now, since the elliptical electron orbits play such an important part in Bohr's newer atomic models, it is natural to consider that possibly the valence electrons of homopolar compounds also describe elliptical orbits in which both foci are occupied by the nuclei of the atoms which are to be united (see, for example, KNORR, C. A., *Z. anorg Chem*, **129**, 109 (1923)). If this idea is applied to the hydrogen molecule, it is found that there will be only one 1_0-ellipse, *i e*, a completely flattened out orbit, because every higher-quantum orbit gives much too low values for the heat of dissociation. In general, however, this sort of system cannot be objected to on the ground that a 1_0-orbit is always impossible because it would lead to collision with the nucleus. In molecules the 1_0-orbit is certainly distorted and therefore is not quite a straight line In the particular case of the hydrogen molecule, a collision between the electron and the nucleus would be avoided; for example, due to a rotation of nuclei about their common center of gravity which is most probably always present (null point energy). (See EUCKEN, A., *Naturwissenschaften*, **10**, 533 (1922).)

It will not be possible to decide whether or not one of the previously advanced models for the hydrogen molecule is correct until the law which describes the mutual influence of rapidly moving electrons is discovered. Under these circumstances an attempt to find models for the homopolar compounds of the higher atoms is still less promising, since, as a rule, even more than two electrons will be shared between the nuclei. Some idea of the complexity of the relations in these homopolar compounds is given by the band spectra; for example, the absorption band spectrum of iodine shows that even at room temperature only a part of the molecules are in the normal state and that at the same time a large number of them are present in various states of excitation.

354. Work Involved in Severing Organic Bonds.[1]—In order to calculate theoretically the unsolved problem of the physical properties of a homopolar bond from the molecular model and to obtain as broad an empirical foundation as possible, it is important to determine a number of constants which are characteristic for the individual homopolar bonds. Bonds of special interest occur in organic compounds; above all, we shall be concerned with those bonds in which carbon is a member; C—H, C—C, C=C, C≡C. Since these bonds do not occur alone, but together with others in the structure of the larger organic molecules, the first problem is to derive the results which hold for the individual bonds from the observations made upon the compounds as a whole.

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[1] See FAJANS, K., *Ber Deut chem Gesell*, **53**, 643 (1920).

One of the most important constants of a bond is the work required to sever it. Even with complex molecules, the determination of this work is not so very difficult if· it is assumed that the work of decomposing such a complex molecule into atoms is purely the sum of the amounts of work involved in separating the individual bonds contained in the compound, *i.e.*, that the work of separating each bond is independent of the neighboring bonds. Therefore it is assumed, in contrast with the heteropolar, that *in the homopolar compounds each atom exercises forces which affect only its immediately neighboring atoms.* As it will be shown later, this assumption is really justified.

Empirically, the work required to decompose a molecule is obtained from the heat of formation at absolute zero, the latter in an emergency being found from the heat of combustion[1] (see **200**). Of course the heat of formation refers to the origin of the compound from solid carbon (diamond) and the diatomic gases (H_2, O_2, etc.); in order to get the work of decomposition, the heat of formation must be increased by the heat of evaporation of carbon (according to the number of carbon atoms in the compound) and the heat of dissociation of the diatomic gases concerned. For each *two* atoms in the compound, the heat of dissociation enters *once* into the calculation.

The heats of formation of a number of hydrocarbons, determined in this manner, are summarized in column 5 of the following table; the heat of evaporation of carbon was taken as 150 *Cal.* (H. Kohn),[2] the heat of dissociation of H_2 as 90 *Cal.*

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[1] As a rule, no great error is introduced when the value determined at room temperature is used

[2] *Z. Physik.*, **3**, 143 (1920).

TABLE 78.—ENERGY OF FORMATION OF SEVERAL HYDROCARBONS (*Calories*)

1 Substance	2 Formula	3 Heat of combustion at constant volume	4 Heat of formation from diamond and H_2	5 Energy of formation from the atoms, obs	6 Number of linkages					7 Heat of formation from the atoms, calc.
					C—H	C—C aliph	C—C arom.	C=C	C≡C	
Methane	CH_4	211	+18	348	4					348
Ethane	C_2H_6	370	+21	591	6	1				592
Propane	C_3H_8	525	+28	838	8	2				836
Tetramethylmethane	$C(CH_3)_4$	845	+32	1322	12	4				1324
n-octane	C_8H_{18}	1308	+55	2055	18	7				2055
Ethylene	$CH_2{=}CH_2$	340	−16	464	4			1		466
Propylene	$CH_3.CH{=}CH_2$	494	− 8	712	6	1		1		710
Acetylene	$CH{\equiv}CH$	312	−56	344	2				1	339
Allylene	$CH_3.C{\equiv}CH$	472	−54	576	4	1			1	582
Benzene	C_6H_6	785	−15.5	1155	6		6			1152
Toluene	$C_6H_5CH_3$	943	−11.0	1399	8	1	6			1396
Naphthalene	$C_{10}H_8$	1247	−32	1828	8		11			1851

The determination of the work of decomposition or the energy of formation no longer offers any difficulties: the linkage C—H is obtained from the energy of formation of methane, which has four such bindings and no other kinds; the linkage C—C is obtained from ethane, etc. Thus the following values are derived:

BOND	WORK OF DECOMPOSITION (PER MOLE) *Calories*
C—H	87
C—C aliphatic	70
C—C aromatic	105
C=C	118
C≡C	170

The agreement between the observed values and those calculated from the above individual values is so satisfactory that one may consider the basic assumption, that the binding energies are quite independent of each other, to be essentially justified. Only naphthalene shows a marked deviation; but in this case the benzene bonds are so increased that a certain mutual effect does not seem surprising.

The values for the work of decomposition of individual bonds are remarkable in many respects:

1. The work of decomposing C—H is, as far as can be judged at the present time, about as great as that for H—H.

2. *The work of decomposing* C—C (*aliphatic*) *is about one-half as much as the heat of evaporation of carbon.* If, in agreement with the results of X-ray analysis (see 358) with respect to the atomic structure of the diamond, it is assumed that each atom of the diamond is linked to four neighboring atoms, then there exists a total of $\frac{4}{2}$N linkages in a gram-atom of diamond, since each single linkage belongs to two atoms. Therefore, in order to evaporate one gram-atom of diamond, 2N linkages must be severed The fact that the work of decomposing the aliphatic bond C—C per mole is approximately half the heat of vaporization of carbon thus makes it probable that *the C atoms in the diamond are held together by the same forces as in the aliphatic compounds*

3. *The work of decomposing the double and triple carbon bonds is greater than that of the single bonds,* although the amounts are far from being twice and three times the latter. This result seems to contradict the viewpoint of organic chemistry, in which, according to experience, it is customary to consider the double and triple carbon bonds as being looser than the single bonds [1] Yet this view is based only upon the fact that a double bond is relatively easily changed to a single bond by the addition of another atom, such as bromine; concerning the absolute value of the strength of a double bond, nothing further can be said here. That the value 118 *Cal* is quite plausible for the bond C=C may be illustrated by the following example Ethylene changes to ethylene bromide by the addition of bromine The molecular heat of reaction is about 26 *Cal.* In order to effect the addition, energy must first be employed, 46 *Cal* to decompose the Br_2 molecule into Br atoms, and $118-70 = 48$ *Cal* to change the double bond into a single one—a total of 94 *Cal* The reason why the reaction takes place in spite of this lies in the relatively high binding energy of bromine and carbon, which from the heat of formation of methyl bromide has a value of about 62 *Cal.* Instead of the observed value of 26 *Cal* for the molecular heat of reaction in the addition of bromine to ethylene, the calculated value is found to be $-94 + 2 \times 62 = 30$ *Cal*

4. The aromatic C—C linkage is considerably stronger than the aliphatic, but it is, however, not so strong as the double bond

Just as the energy of formation of a compound may be calculated from the work of decomposing the individual linkages, it is, of course, possible to calculate back from them to the heat of combustion, provided the heat of evaporation of carbon, the heat of dissociation of hydrogen, and the heat of combustion of both carbon and hydrogen are considered as being known

355. Light Absorption and Color of Organic Compounds.—Further empirical material on the mutual bonds between molecules is given by the optical properties of substances.

Direct information concerning the energy transitions and, therefore, also concerning the orbits of the valence electrons is furnished, as has already been mentioned in **335**, by the characteristic emission or absorption spectra of molecules in the gaseous state which are usually called the band spectra.

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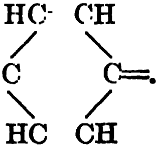
[1] * Not all organic chemists accept this viewpoint; some consider, rather, that a double bond is not so strong as two single bonds, etc.

If the absorption of a substance in the liquid or dissolved state is observed, all the fine structures of the band spectra disappear and only a reduced number of relatively broader absorption regions is left. Although these absorption spectra are less suitable for a quantitative investigation of the molecular structure than the band spectra of the gases, it is possible to deduce from them a number of valuable empirical laws for the investigation of the constitution of organic molecules.

Even without a spectral investigation, the color of a compound gives a certain indication concerning the approximate position and strength of the absorption bands in so far as these lie in the visible portion of the spectrum. A blue-colored solution, for example, absorbs in the orange region; a yellow solution in the blue-violet, etc.

The majority of valence electrons of simple homopolar bonds in the unexcited state of the molecule (*i.e.*, at ordinary temperatures) generally have relatively high velocities of revolution and, therefore, similar to the Lyman series of hydrogen, can get into the next neighboring stable orbit only by a large energy transition, that is to say, by the absorption of ultra-violet light. An absorption in the visible spectrum is obtained from electrons whose energy transitions are smaller and, therefore, also possess smaller velocity of revolution than the normal valence electrons.

An absorption in the visible region is thus to be expected in linkages containing relatively loosely bound electrons, which is frequently discerned by chemical means from the unsaturated character of the bonds. Indeed, a number of unsaturated groups of atoms may be named, in the presence of which a coloring of the molecule always occurs, and which are usually called **chromophores** (O. N. Witt). Examples of such chromophores are found in the groups $=C=O$, $=C=S$, $=C=N-$, $-N=N-$, and especially



If the chromophore group is relatively weak, as, for example, the carbonyl group, then a single group is not sufficient to develop a visible color in the molecule and two or more are necessary. Thus the effectiveness of groups is very much greater when they are immediate neighbors. As a rule, the color caused by one or more chromophore groups is changed by introducing still another group (which of itself will not develop a color) into the molecule; these are distinguished as the **bathochrome groups** (*e.g.*, —CH_3, —O—CH_3, —COOH, —C_6H_5, etc), which displace the absorption spectrum from violet toward the red and therefore cause color changes from yellow to green through red, blue, and violet; and the **hypsochrome groups** (*e.g* , —H), which work in the opposite direction. Moreover, in order to transform a compound, which is colored due to the presence of a chromophore group, into a real dye which has the property of clinging fast to organic fibers, it is, in general, necessary to introduce still another group, the **auxochrome** (*e.g.*, —NH_2, —OH), which always acts as a bathochrome at the same time.

However, recent exhaustive investigations[1] indicate that the simple assumption of a simple chromophore group which is more or less influenced by other groups does not always suffice for the explanation of the *origin* of colored organic compounds.

In agreement with the above assumption of the presence of loosely bound electrons, a color seems to appear not only when single chromophores are present, but also when the whole molecule seems to be chemically somewhat loosened (Kauffmann calls this phenomenon "Valenzzersplitterung"), even without the presence of definite chromophore groups. The benzene ring in particular is easily affected by such an influence, since, according to Kauffmann, it is capable of existing in a large number of states which can be converted into each other rather easily. Thus it is clear that sometimes a color can appear or disappear through apparently trifling changes within the molecules. Examples of this are found especially among the indicators, *i.e.*, basic and acidic dyes which in the undissociated and ionized states have totally different colors (see **191**). Since the mere addition of an H^+ or an OH^- ion cannot, according to other experience, directly produce a change of color, it must be assumed that the dissociation of an indicator involves a more or less extensive internal rearrangement, which is to be considered as the real reason for the change of color. In a number of cases, as Hantzsch has shown, such rearrangements may be demonstrated chemically, or at least be made very probable.

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[1] An excellent review of these investigations is given by HENRICHS, F., "Theories of Organic Chemistry," translated by JOHNSON and HAHN, John Wiley & Sons, Inc. (1922).

356. Molecular Refraction.—Besides the emission and absorption phenomena, the electrons contained in a molecule make themselves conspicuous by *an influence on the velocity of propagation of light* passing through the substance. The substance thus shows, compared with a vacuum, a bending of the light ray (refraction), and the influence becomes greater the more closely the vibration number of the light ray approaches the frequency of the electron.

We are, therefore, interested in finding a quantity which in the simplest possible manner will express the influence of the individual electrons (valence and others) contained in the molecule. It is seen at once that the relationships in this case will be somewhat more complex than for the heat of formation of a molecule, which could be obtained in a simple additive manner from the energy values characteristic of the specific linkages involved. That the refractive index of a compound cannot be made up additively from the indices of its constituents is shown by the simple fact that atomic carbon (diamond) has a much higher refractive index than any organic compound.

Theory[1] teaches that the refractive index (n_r) of a substance must be represented by the expression

$$n_r = \sqrt{1 + \frac{4\pi(N'A' + N''A'' + \cdots)}{1 - \frac{4\pi}{3}(N'A' + N''A'' + \cdots)}}, \qquad (303)$$

where N', N'', etc. are the numbers of the different kinds of electrons in the unit volume; A', A'', etc. are quantities which depend upon constants of the electrons, especially their characteristic frequencies, as well as the wave length of the light.

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[1] See LORENTZ, H. A., "The Theory of Electrons," Leipzig (1909). The calculation has only been performed on the basis of classical theory, but the application of the quantum theory will not make any essential difference in the results obtained for refraction and dispersion. *See also the chapter by P. DEBYE in MARX, Handbuch der Radiologie (loc. cit.) vol. 6, 1925

By transformation we get

$$\frac{n_r^2 - 1}{n_r^2 + 2} = \frac{4\pi}{3}(N'A' + N''A'' + \ . \ . \ .)$$

or

$$\frac{n_r^2 - 1}{n_r^2 + 2} = \frac{4\pi N'A'}{3} + \frac{4\pi N''A''}{3} \ . \ . \ .$$

It is desirable to have this expression in molar terms rather than in cubic centimeters, *i.e.*, to multiply it by the molecular volume $v_m = \frac{M}{\delta}$. The quantities $v_m N'$, $v_m N''$, etc. then become equal to **N**, Avogadro's number, provided that in each molecule there occurs just one of each kind of electron concerned, or a whole number (a_1, b_1 . . .) times **N**, if each molecule contains more (a_1, b_1, . . .) electrons of each sort. Putting $\frac{4\pi}{3}A'\mathbf{N} = A_1$; $\frac{4\pi}{3}A''\mathbf{N} = A_2$, then each of the quantities A_1, A_2, etc. represents, for a definite wave length of the light, a constant quantity which has a value characteristic for every electron (valence as well as interatomic) vibration and for every wave length, and which is called the **refraction equivalent.** Hence,

$$\frac{n_r^2 - 1}{n_r^2 + 2}\frac{M}{\delta} = a_1A_1 + b_1A_2 + \ . \ . \ . \qquad (304)$$

The expression $\frac{n_r^2 - 1}{n_r^2 + 2}\frac{M}{\delta}$, which is called the **molecular refraction,** *is thus composed additively of the refraction equivalents of the individual electronic vibrations.*

In order that it may be a really additive property of the individual electron vibrations the molecular refraction must above all be independent of the state of aggregation or the density (temperature) of the substance. As Table 79 shows, this condition is, indeed, fulfilled. Another somewhat simpler expression, $\frac{n_r - 1}{\delta}$, also varies but slightly with the density.

Experience shows further that the molecular refractions may really be calculated additively in a fairly satisfactory manner

TABLE 79

Substance	$\frac{n_r - 1}{\delta}$			$\frac{n_r^2 - 1}{n_r^2 + 2} \cdot \frac{1}{\delta}$		
	Vapor	Liquid	Difference	Vapor	Liquid	Difference
Water	0 3101	0 3338	−0 0237	0 2068	0 2061	+0 0007
Carbon disulfide	0 4347	0 4977	−0 0630	0 2898	0 2805	+0 0093
Chloroform	0 2694	0 3000	−0 0306	0 1796	0 1790	+0 0006

from specific, empirically determined refraction equivalents. As is to be expected from the foregoing, a definite refraction equivalent is generally to be introduced for each atom as well as for each bond. If the atom or bond concerned occurs *a* times in the molecule, its equivalent is to be multiplied by factor *a*.

A number of refraction equivalents for the calculation of the molecular refraction of organic substances are given in Table 80. In most cases the equivalent of the atom concerned is combined with that of its bond to a C atom, to give a single number. For the bond C—C, the value zero should be assumed in accordance with the data in the previous literature, although in this way the molecular refraction of the simplest hydrocarbons (CH_4, C_2H_6) is not quite correctly reproduced[1]

TABLE 80.—REFRACTION EQUIVALENTS FOR VARIOUS COLORS

Substance	H_α	D	H_β	$H_\beta - H_\alpha$
Carbon.	2 413	2 418	2 438	0 025
Hydrogen .	1 092	1 100	1 115	0 023
Carbonyl oxygen ..	2 189	2 211	2 247	0 057
Ether oxygen.	1 639	1 643	1 649	0 012
Hydroxyl oxygen. .	1 522	1 525	1 531	0 006
Chlorine .	5 933	5 967	6 043	0 107
Bromine .	8 803	8 865	8 999	0 211
Iodine... .	13 757	13 900	14 224	0 482
Ethylene bond ..	1 686	1 733	1 824	0 138
Acetylene bond	2 328	2 398	2 506	0 139

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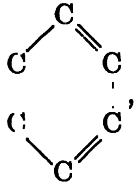
[1] Satisfactory results are obtained if the value 0.27 is used for C—C, and 2 20 for the C atom; the values for ethylene and acetylene bonds are then to be increased by 0.27.

As an example, the calculation of the molecular refraction of ethyl alcohol from the observations and from the refraction equivalents may be compared. The refractive index for the sodium D-line is 1.361, the density 0.791, and therefore the molecular refraction is 12.89, while the sum of the refraction equivalents is $2 \times 2.418 + 6 \times 1.100 + 1.525 = 12.96$.

The molecular refraction for benzene, strange to say, may be calculated according to the old Kékulé formula , by using the refraction equivalent for the double bond three times. Since this formula is to be considered as disproved, it would be more correct to introduce a special refraction equivalent for the benzene bond which must be about one-half as large as that of the ethylene bond.

With complex molecules there sometimes occurs a marked excess ("exaltation") of the observed molecular refraction above that calculated from the refraction equivalents. Deviations occur, especially when two double or triple bonds are separated by only one single bond. For such *conjugated bonds* other refraction equivalents must, therefore, be introduced, which are somewhat different from those of single bonds or of more widely separated double bonds.

It thus seems as if the principle that the molecular refraction can be calculated from the refraction equivalents of the atoms and quite definite bonds alone is, indeed, approximately correct but cannot be applied rigorously. In cases where it fails to work one must assume that there is an influence of the neighboring bonds—which, according to the results given in **353**, is not to be wondered at, especially with the greater anomalies (double and triple bonds); with two conjugated double bonds, the "exaltation" is considerably affected, so that the single bond between them is weakened and its refraction equivalent increased. The comparison of the observed and calculated molecular refractions is frequently used to aid in the investigation of the constitution of compounds in organic chemistry. The sensitivity of the molecular refraction, as compared with the influence of constitution, is especially valuable in this connection.[1]

The refractive index and, therefore, also the molecular refraction of a substance changes with the wave length of the light; thus the substance shows the phenomenon of *dispersion.* The difference of the molecular refractions of a substance for different wave lengths is called the **molecular dispersion.** It can be shown that this, just as the molecular refraction, is composed of *dispersion equivalents* which are characteristic of the individual atoms and bonds (see Table 80, column 5). For the investigation of the constitution, the determination of the molecular dispersion is often even more useful than that of the molecular refraction.

d. THE FORMATION OF CRYSTALS

α. The Structure of Crystals

357. The Arrangement of the Atoms or Molecules of a Crystal in a Space Lattice.—From the standpoint of the atomic theory it was suggested, even without a more exact knowledge of the details, that the striking regularity of crystals was to be explained by a similarly regular arrangement of the atoms or molecules. As early as 1850, Bravais was able to express the conjecture that a crystal could be conceived of as a more or less complex space lattice in which atoms or molecules were placed at the points of intersection. By mathematical-geometrical treatment, this conception was later systematically extended by Fedorow (1890) and especially by Schonflies (1891); they derived the structures of the various molecular or atomic space lattices from the perceptible properties of the crystals (the position of the crystal surfaces, symmetry, etc.). The investigations were based upon the directly plausible assumption that a crystal surface could be formed only in such a direction as a plane ("Netzebene" or **atomic plane**) could be located in the space lattice; this plane passed through a large number of points of intersection at which the atoms and the molecules were situated. In an ordinary cubic lattice it is possible to locate such planes not only parallel to the surfaces of the cube but also perpendicular to the diagonal of the cube (which gives the octahedral surface of regular crystals), as well as perpendicular to the diagonals of the faces.

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[1] See EISENLOHR, "Spektrochemie organischer Verbindungen," Stuttgart (1912); also HENRICH, *loc. cit.*

A direct confirmation of the conception of a space lattice was first obtained through the discovery by Max von Laue (1912) (see **322**) that *the space lattice of the atoms in crystals could be used as a "diffraction grating" for the X-rays.* After that it was possible not only to solve the problem of measuring the wave lengths of the X-rays when the dimensions of the space lattice were know, but also the converse problem of determining the space-lattice arrangement of unknown crystals in case X-rays of definite wave lengths were used.

358. The Determination of the Atomic or Molecular Space Lattice by Means of X-rays of Known Wave Length.[1]—For the analysis of the space lattice Bragg's reflection-angle method, already briefly discussed in **322**, is very suitable. The reflection angles for different (at least three) crystal surfaces are determined, and from these the distances between the planes occupied by the atoms or molecules may be calculated by the application of Eq. (284). These planes obviously correspond to distinctive planes in the space lattice. Thus if a number of the planes belonging to the various crystal surfaces are constructed, in the ratio of the measured distances, then the intersection points of the space lattice and the position of the atoms or molecules are obtained.

If the planes corresponding to a crystal surface are not equally spaced and contain different atoms, the separation and the approximate content of the two planes can be determined if the reflected rays of higher order are considered, *i.e.*, if not only the angle corresponding to $\frac{\lambda}{d} = 2 \sin \alpha_1$ is used but also $\frac{\lambda}{d} = \frac{2 \sin \alpha_2}{2}$, $\frac{2 \sin \alpha_3}{3}$ . . . By way of example it might be assumed that we are concerned with two planes I and II, which are occupied by about the same masses and which follow each other alternately; the distance between the planes I-I may be considered to be related to that between II-I as 3 to 1.

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[1]* BRAGG, W. H and W. L., "X-rays and Crystal Structure,"* WYCKOFF, R. W. G, "The Structure of Crystals"; Chemical Catalog Co. 1924., EWALD, P., "Kristalle und Rontgenstrahlen."

The two rays reflected from the different planes, in general, vibrate in different phases, at one time being strengthened, at another time weakened by interference. To illustrate the prevailing relations, turn to Fig. 92, in which, of course, the waves are not sketched with their reflection angle but with the projection of this on the ordinate. Thus, for the example chosen, the second-order reflection angle is completely eliminated, but the fourth order is intensified. The determination of the structures of several simple crystals according to this procedure has been explained in a clear fashion by W. L. Bragg.[1]

The Bragg rotating-crystal method, which has the disadvantage of requiring relatively large crystal surfaces, has been modified by Debye and Scherrer and independently also by Hull,[2] so that a finely divided crystal powder can be used. The X-rays of a definite wave length are allowed to fall upon a small cylinder, which consists of the crystalline material or into which the crystal powder is pressed. In case the positions of the small crystals are completely disordered, a number of the crystal surfaces will be in the positions of their reflection angles, and reflection will occur. The rays reflected in the various directions are most

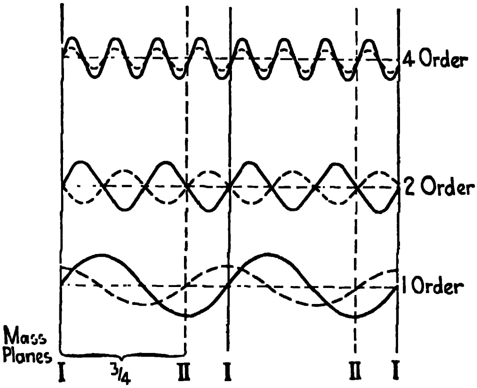

FIG 92

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[1] *Proc Roy Soc. A*, **89**, 248 (1913); also BRAGG, W. H. and W. L., "X-rays and Crystal Structure," chap. VIII, *et seq.*

[2] See BRAGG, W H. and W. L., "X-rays and Crystal Structure," chap. X.

simply registered by surrounding the crystal cylinder by a cylindrical photographic film (see Fig. 93). From the size of the angle at which the original ray is reflected, the reflection angle of the plane is found directly. In spite of the fact that in complex crystals the various crystal surfaces usually have different reflection angles, all of which appear simultaneously on the photographic film, an unequivocal evaluation of these is not, as a general rule, possible without other information.

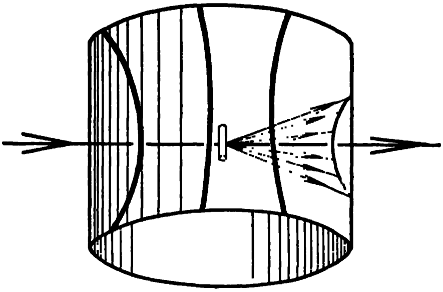

FIG 93

359. The More General Results of Crystal-structure Determinations by Means of X-rays.

359. The More General Results of Crystal-structure Determinations by Means of X-rays.—The X-ray analysis not only gives the space-lattice arrangement of numerous crystals but leads also to several results of more general importance, of which the following may be emphasized:

At the equidistant lattice points of rock salt and the related salts (KCl, KBr, etc) atoms or ions, and not molecules, are found. The X-ray analysis shows, first, that the mass centers of the atoms or molecules are arranged in an ordinary cubic space lattice, such as is represented in Fig. 94.[1] At the same time, the lattice distance Δ_0 of the space lattice is obtained. If Eq. (255) is now applied, we find for the molecular volume: $v_m = \mathbf{N}\Delta_0^3$, if the lattice points are occupied by molecules, or $v_m = 2N\Delta_0^3$, if they are occupied by atoms. Since the lattice distance Δ_0 as determined[1] by the X-ray analysis is $2.815 \cdot 10^{-8}$, in the first case $v_m = 13.50$ and in the second 27.00 are obtained, while from the molecular weight and the density $\frac{58.5}{2.17} = 27.00$ *cc.* is obtained. *The lattice points are therefore occupied either by atoms or by ions.*

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[1] It may be assumed in this case that all the mass centers of the lattice, and therefore all planes, are approximately equally effective (*e g* , KCl). If the crystal is built up of atoms or ions of different weights, the planes of the octahedral surfaces, which consist alternately of the two kinds of atoms or ions, will be unequally effective in reflecting the X-rays. Investigation has confirmed the inequality of the planes of the octahedral surfaces for the majority of salts, and, therefore, has proved directly that the building units of the crystals involved cannot all be of the same sort, which would be the case if the lattice points were occupied by molecules instead of atoms or ions.

A number of arguments may be advanced in favor of the idea that the lattice points are occupied by ions and not by atoms:

1. The fact that the characteristic atomic vibrations can be made electromagnetically perceptible by means of the so-called residual rays (see **79**), which is only possible if the atoms are ionized.

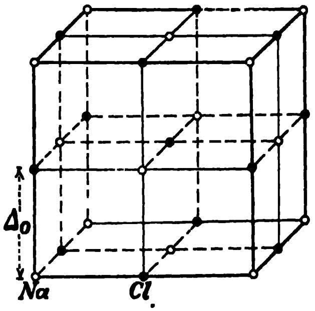

FIG. 94.

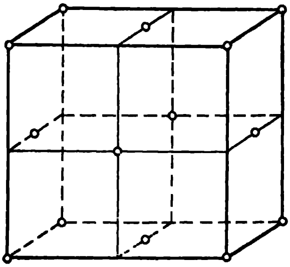

FIG. 95

2. The fundamental conception of the nature of heteropolar compounds.

3. Electrolytic dissociation.

4. The confirmation of the magnitude of the lattice energy which is to be calculated in **361**.

5. According to Debye, the intensity of an X-ray beam diffracted from atoms depends upon the number of their outer

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[1] In order to be able to find an unknown lattice distance (or parameter), the wave length of some line in the X-ray region of the spectrum must be accurately determined. In principle, this is done by proceeding from a lattice that is certain to be monatomic (like the diamond or metals) and calculating the lattice distance from the molecular volume according to Eq (255). The wave length can then be found from this value and the measured reflection angle by using Eq. (284).

electrons. Now, since the X-ray beam reflected through the reflecting angle represents a measure for the diffracting power of the atoms in the various planes, Debye was able to draw certain conclusions concerning the number of electrons occurring at the individual lattice points from the intensity of the various reflection orders of the X-rays reflected from the LiF crystal. He found that the number of electrons corresponds to the ions, not to the neutral atoms.

Even though these arguments, taken individually, could not be considered as quite conclusive, taken all together, the result that ions and not atoms are situated at the lattice points in most salts is quite beyond any doubt. In some salts like $HgCl_2$, which are very slightly dissociated electrolytically, the residual rays are also extraordinarily weak; in such cases either neutral atoms or whole molecules must be situated at the lattice points.

360. The Lattice Structure of Certain Crystals.—While the two ions of a simple binary salt commonly form an ordinary cubic lattice (Fig. 94), a large number of metals have the so-called *face-centered cubic lattice* (Fig. 95), which arises from the simple cubic lattice by merely removing each second point. A few of the metals (Li, Na, Fe) have the *cube-* (*or body-*) *centered lattice* (Fig. 96), in which one extra atom is situated in the center of each cube whose corners are occupied by atoms; this lattice can be considered as being formed by the interpenetration of two simple cubic lattices with a doubled value of Δ_0. A number of other metals (like Mg, Cd, Zn, Hg) crystallize in the hexagonal system, a structure which usually approaches the most dense packing (of spheres) possible.

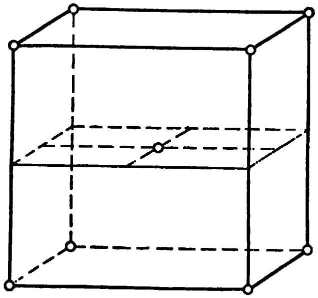


FIG 96

The structure of the diamond (Fig. 97) is more complex than that of rock salt. One may imagine it as consisting of two face-centered cubic lattices which have been displaced along one of the cube diagonals a distance of one-quarter the length of the diagonal The structure is very much clearer if the tetrahedral arrangement is considered as the base, and from this it can be seen that each atom in the diamond is located at the center of a tetrahedron whose corners are also occupied by carbon atoms, so that each carbon atom is bound equally in all four directions corresponding to the four valence bonds.

Graphite (Fig. 98) has a crystal structure which is quite different from that of the diamond. It consists of a number of hexagonal rings (benzene rings) bound together in one plane, these planes being arranged in layers above each other and relatively far apart. On this account they are relatively loosely held together, and hence the ready cleavage of graphite along these planes. It may also be considered that graphite would be transformed into diamond if the large, perpendicular connections of the C atoms between the various layers were greatly shortened, *i.e.*, if the carbon atom involved was caused to leave the plane of the hexagon by being raised or lowered. (According to Debye and Scherrer, lampblack consists of very fine graphite splinters.) This structure agrees very well with the chemical fact that in the oxidation of graphite or soot mellitic acid is formed.

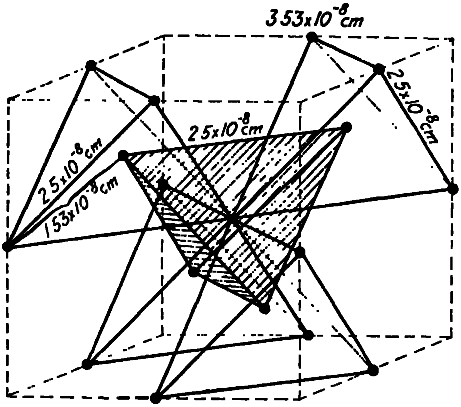


FIG. 97.

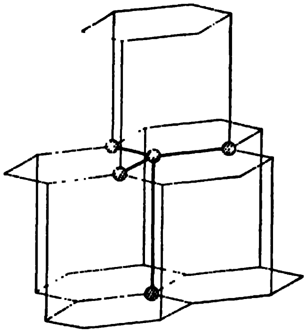
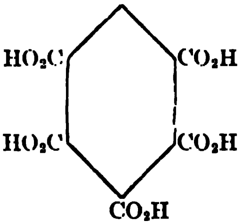
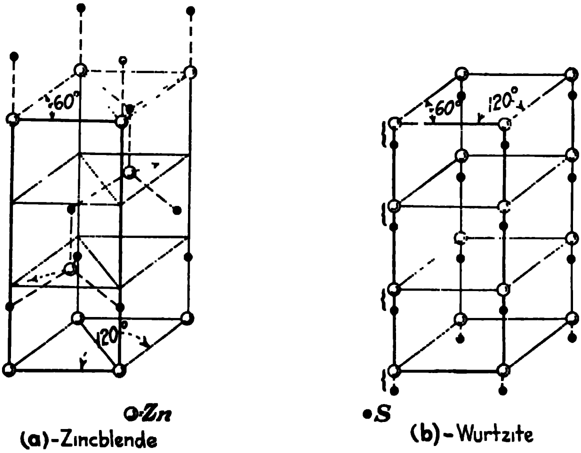


FIG. 98.



Zincblende possesses the same sort of structure as the diamond, except that Zn and S atoms follow each other alternately. An S atom is found in the center of each tetrahedron the corners of which are occupied by Zn atoms, and, conversely, each Zn atom is surrounded by four S atoms (*cf.* Fig. 99*a*, and 97).

Zincblende, which belongs to the regular system, bears the same relation to the hexagonal modification of ZnS (wurtzite) as diamond does to graphite. The space lattice of wurtzite which is illustrated by Fig. 99*b* is of particular interest, because in contrast with zincblende the atoms approach each other so closely in pairs that it is really possible to speak of the formation of a molecule in this case. As is indicated by Figs. 99*a* and *b*, wurtzite can be considered as being formed from zincblende in the following way: take the two parallel neighboring layers in which Zn and S atoms are directly perpendicular to each other and displace them in the direction indicated by the arrow (Fig. 99*a*), so that all atoms come to lie directly over each other.



(a)-Zincblende (b)-Wurtzite

Fig 99

β. The Lattice Energy of Crystals of Heteropolar Compounds

361. Electrostatic Calculation of Lattice Energy.—On the basis of the fact that ions are located at the lattice points of rock-salt crystals and from the models of monovalent ions given in **350**, it is possible, as Born and Lande[1] have shown, to determine the forces acting between the ions and from these forces the energy which would be obtained if gaseous ions were allowed to unite into a crystal. This energy is called the **lattice energy.** It thus involves a detailed calculation, depending upon electrostatic laws, of those attracting and repelling forces whose presence has already been proved (**68**) to be essential to the understanding of the solid state, but whose more detailed properties could not be determined at that time.

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[1] *Verh. Deut physik Gesell*, **20**, 210 (1918); Born, M., *ibid*, **21**, 553 (1919). A simple presentation is given by Born, M, "The Constitution of Matter," translated by Blair and Wheeler, E. P. Dutton & Company (1923).

In the calculation of the attractive force, to which is ascribed a greater effective range than the repulsive force, the ions are considered, as a first approximation, to be simply charged spheres. Between two single, differently charged ions Coulomb's law $\frac{e^2}{\Delta}$ is considered to hold; Δ is the distance existing for the moment between the ionic centers, which in a simple cubic lattice is the same as the distance between the planes of the cube faces. In the ionic lattice each ion is acted upon simultaneously from all sides by a large number of positively and negatively charged neighboring atoms, by which the force as a whole becomes somewhat diminished. As an exhaustive calculation by E. Madelung[1] shows, the attractive force between two neighboring ions in the direction of the line connecting them is:

$$\mathfrak{K}_a = -0.2905\frac{e^2}{\Delta^2}.$$

The work required to separate a single connection completely when the original distance was Δ_0, is, therefore,

$$\phi_a = 0.2905\,\frac{e^2}{\Delta_0}\cdot \qquad (305)$$

In order to separate the ions of a whole crystal containing one mole of the compound and therefore 2N ions, a total of $6/2 \times 2\mathbf{N} = 6\mathbf{N}$ connections must be broken (from each ion six connections proceed, but only half of them are involved in the calculation). The positive part of the lattice energy per mole thus amounts to

$$\phi_a = \frac{1.743\mathbf{N}e^2}{\Delta_0}\cdot \qquad (305a)$$

If the value of Δ_0 for rock salt is introduced, we get

$$\phi_a = \frac{1.743 \times 6.06 \times 10^{23}(4.77 \times 10^{-10})^2}{2.815 \times 10^{-8}} = 848 \cdot 10^{10}\ \mathit{ergs} \simeq 200\ \mathit{Cal.}$$

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[1] *Physik Zeit.*, **19**, 524 (1918).

or, more generally, putting

$$\Delta_0 = \sqrt[3]{\frac{M}{2\mathbf{N}\delta}}$$

then

$$\Phi_a = 613\sqrt[3]{\frac{\delta}{M}}\ Cal. \qquad (305b)$$

If the outer electron shells are considered simply as rigid elastic spheres, then the calculation of the lattice energy ends with the expression Eq. (305*b*), which may be said to be sufficient as a first approximation.

In other cases—for example, in the calculation of the compressibility of the crystal lattice—the repulsive force ($\mathfrak{K}_r$) of the ions, which is due to the mutual effects of the negatively charged electron shells, must be considered as well as the attractive force. In this case it is, of course, necessary to turn back to a detailed model of the ions. By considering the ions of the halogens or alkali metals as cubes whose corners are occupied by eight electrons with the inside carrying an effective positive charge of seven or nine, Born succeeded in finding a repulsive force (limited by the mutual effects of the outer electrons) which increases inversely proportional to the tenth power of the distance. Thus the repulsive force is to be calculated from the centers of the cubes just like the attractive force, and, therefore, the following equation is found, which, however, can be expected to hold only for a very limited range

$$\mathfrak{K}_r = \frac{\beta}{\Delta^{10}}.$$

The value of the factor β may be empirically determined by assuming that, when the atoms are in the position of rest, the repulsive force must be equal to the attractive. Therefore we may put

$$\frac{\beta}{\Delta_0{}^{10}} = \frac{0.2905e^2}{\Delta_0{}^2},$$

or

$$\mathfrak{K}_r = \frac{0.2905e^2\Delta_0{}^8}{\Delta^{10}}.$$

The total force acting upon an atom outside of the position of rest is, therefore,

$$\mathfrak{K}_a + \mathfrak{K}_r = \mathfrak{K} = \frac{0.2905e^2}{\Delta^2}\left(-1 + \frac{\Delta_0^8}{\Delta^8}\right). \tag{306}$$

The work of separation for *one* bond or connection is, in analogy with Eq. (305):

$$\Phi = \frac{0.2905e^2}{\Delta_0}\left(1 - \frac{1}{9}\right) = \frac{0.2905}{\Delta_0}e^2\frac{8}{9}. \tag{307}$$

The consideration of the repulsive force gives for Eq. (305*a*) also the factor $8/9$, so that in place of Eq. (305*b*) we get:

$$\Phi = 545\sqrt[3]{\frac{\delta}{M}}\,Cal., \tag{307a}$$

a relation which claims to hold approximately for all binary salts of the same crystal type as NaCl, whose ions contain eight electrons in the outer shells and whose repulsive force may be assumed, therefore, to be (approximately) inversely proportional o Δ_0^{10} (the lithium salts are thereby excluded).

362. A Test of the Electrostatically Calculated Lattice Energies.—A test of Eq. (307*a*) is only possible by indirect methods, since a decomposition of an ionic lattice into a completely ionized ideal gas and the measurement of the energy required is not practically feasible. However, certain differences of lattice energies can be readily measured.

For example, the salts NaCl and KI can first be transformed into ionized gases and then the ions considered as uniting to form two other lattices, namely, KCl and NaI. The total difference of energy

$$U' = -\Phi_{NaCl} - \Phi_{KI} + \Phi_{NaI} + \Phi_{KCl}$$

must be equal to the energy of transformation and, therefore, as a first approximation be equal to the heat content of the reaction

$$NaCl_{solid} + KI_{solid} = NaI_{solid} + KCl_{solid}.$$

The latter may be measured indirectly, most surely, by dissolving all the salts to form a very dilute solution in which they are completely ionized. Since the heat of mixing of these solutions is (see **141**) equal to zero, Hess' law (see **200**) gives the heat content of reaction simply from the difference of the heats of solution L.

$$Q = L_{NaCl} + L_{KI} - L_{KCl} - L_{NaI}.$$

In the following table the difference of the lattice energies U' and the heat of solution Q are compared. Since the differences, especially with respect to the lattice energy, amount to only a few per cent of the absolute values, the agreement may be said to be satisfactory.

TABLE 81.—DIFFERENCES OF LATTICE ENERGIES AND OF HEATS OF SOLUTION

Reaction	U' calc.	Q calc.
$KCl + LiBr = KBr + LiCl$	+4	+3 6
$KCl + LiI = KI + LiCl$	+7	+7 2
$KCl + NaBr = KBr + NaCl$	+3	+2 0
$KCl + NaI = KI + NaCl$	+5	+3 4

363. The Calculation of the Work of Ionization for the Chlorine Atoms.—If, in view of the above, the expression for the lattice energy is considered essentially correct, then it can be applied to the calculation of other, more important, but as yet unknown, atomic energy values. For example, the work of ionization of the halogen atoms, which has already been used in **350**, is of outstanding interest. This may be obtained by means of the following cyclic process:

$$\begin{tikzcd}
 & NaCl_{solid} \arrow[dl] \arrow[dr, "\text{(Lattice energy } - \Phi)"] & \\
Na^+ \arrow[d, "J_{Na}"] & & Cl^- \text{ (Ion vapor)} \arrow[d, "J_{Cl} \text{ (Work of ionization)}"] \\
Na \arrow[d, "\Lambda_{Na}"] & & Cl \text{ (Neutral atoms)} \arrow[d, "D_{Cl} \left(\begin{array}{l}\text{Heat of evaporation} \\ \text{or dissociation}\end{array}\right)"] \\
Na_{solid} \arrow[dr, "U'"] & & \frac{1}{2}Cl_2 \arrow[dl, "\text{(Heat of formation)}"'] \\
 & NaCl_{solid} &
\end{tikzcd}$$

The following energy equation is now obtained:

$$-\Phi + J_{Na} + J_{Cl} + A_{Na} + D_{Cl} + U' = 0.$$

If, according to Eq. (307*a*), we put $\Phi = 182$ *Cal.*, J_{Na} from **310** (with $\nu'_\infty = 41445$) is 117 *Cal.*, $A_{Na} = 27$ *Cal.*, $D_{Cl} = 30$ *Cal.* (*per gram atom*), $U' = 98$ *Cal.*, we obtain

$$J_{Cl} = -90 \ Cal.$$

According to this, free chlorine atoms have a negative energy of ionization; this could have been expected from the beginning. The formation of an ion, *i.e.*, the taking up of an electron, thus takes place spontaneously with the liberation of energy. Since with the alkali metals the formation of an ion takes place with the liberation of an electron from the neutral atom and the absorption of energy, and since the absolute amount of the energy involved is but little greater than for chlorine, the total energy of ionization of the metallic salt vapor which is already dissociated into atoms is slight (for NaCl it amounts to about 27 *Cal.*).

364. Calculation of the Compressibility of Several Crystals.—The compressibility of crystals may be calculated as follows from the equation for the total energy of a lattice (Eq. (306)):

While the force vanishes at the position of rest, it immediately assumes noticeable values when the distance Δ_0 is slightly decreased to Δ. If Eq. (306) is differentiated with respect to Δ and then Δ is again put equal to Δ_0 and $d\Delta = \Delta_0 - \Delta$, then it follows that·

$$\mathfrak{R} = \frac{0.2905}{\Delta_0^3} 8e^2(\Delta_0 - \Delta).$$

The amount of work to be performed (from the outside) over the distance $\Delta_0 - \Delta$ thus amounts to:

$$-\int_{\Delta}^{\Delta_0} \mathfrak{R}\, d\Delta = \frac{2.324e^2}{\Delta_0^3} \frac{(\Delta_0 - \Delta)^2}{2}.$$

If a mole is thus compressed so that the distance Δ_0 is decreased to Δ, then this amount of work must be performed 6N times, which gives us the expression

$$A_{Mol} = \frac{13.94 \cdot e^2}{\Delta_0^3} \frac{(\Delta_0 - \Delta)^2}{2} \mathrm{N}.$$

This amount of work is, obviously, to be put equal to the volume work performed by the compression; for the latter we find, since the pressure during the compression is not constant but changes from 0 to *p*, as a first approximation, $\frac{1}{2}p\Delta v_m$. It, therefore, follows that

$$p\Delta v_m = \frac{13.94}{\Delta_0^3} e^2(\Delta_0 - \Delta)^2 \mathrm{N}.$$

Now, since $\Delta_0 - \Delta$ has already been assumed to be small, the cube of this distance is practically zero and we may put

$$(\Delta_0 - \Delta)^3 = \Delta_0^3 - \Delta^3 - 3\Delta_0^2\Delta + 3\Delta^2\Delta_0 \simeq 0$$

or

$$\Delta_0^3 - \Delta^3 = 3\Delta_0\Delta(\Delta_0 - \Delta) \simeq 3\Delta_0^2(\Delta_0 - \Delta).$$

Since $2N(\Delta_0^3 - \Delta^3) = \Delta v_m = 2N3\Delta_0^2(\Delta_0 - \Delta)$, it follows that

$$p = \frac{13.94}{\Delta_0^7 \cdot 36}\,\frac{\Delta v_m}{N}\,e^2.$$

For the compressibility κ, which is here to be put equal to $\frac{1}{v_m}\frac{\Delta v_m}{p}$, we finally get:

$$\kappa = \frac{\Delta v_m}{2N\Delta_0^3 p} = \frac{18\Delta_0^4}{13.94e^2} = 5.68 \times 10^{18} \cdot \Delta_0^4.$$

The test of this extremely simple formula, according to which the compressibility of a binary salt depends only upon the lattice constant Δ_0, using the experimental material, leads to a striking confirmation, as the following table shows[1]

TABLE 82.—COMPRESSIBILITY OF CERTAIN CRYSTALS

	κ obs	κ calc.
NaCl ..	4.1×10^{-12}	3.46×10^{-12}
NaBr .	5.1	4.73
NaI .	6.9	6.30
KCl	5.0	5.36
KBr ..	6.2	6.64
KI .	8.6	8.68
TlCl	4.7	4.69
TlBr	5.1	5.36
TlI	6.7	6.76

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[1] * Richards and Saerens (*J. Am. Chem. Soc.*, **46**, 934 (1924), while acknowledging that Born's equation for the compressibility is in the right direction, point out a number of discrepancies in it, including the fact that Born does not adequately take into account the affinities which bind the atoms together to make the solid. In this paper will be found numerous references to work on the compressibilities of salts. (See also SLATER, J. C., *Phys. Rev.*, **23**, 488 (1924).)

365. Summary.—Just as it was possible, by means of purely electrostatic forces, to determine a number of chemical properties of heteropolar molecules on the basis of very simple assumptions, an attempt to calculate in an analogous manner some important properties of crystals of heteropolar compounds has also proved successful. Thus, on the whole, *evidence has been produced for at least the heteropolar substances that the so-called chemical forces are identical with the forces which determine the coherence of the crystal.* That the existing theory cannot yet reproduce all the details is not surprising in view of the quite schematic atomic model involved in the considerations.[1]

The relations in the purely homopolar compounds are far more unsatisfactory, but even here it could certainly be shown, at least for the diamond, that the chemical forces are identical with the cohesive forces of the crystal (see **354**). However, a satisfactory calculation of these forces on the basis of theoretical conceptions has not yet been attained in any conclusive way, even for the simplest compounds.

The investigations on the more complex molecules have been more successful than those on the simpler compounds. According to a theory developed by Debye,[2] the force of attraction (van der Waals) of such molecules reduces to a sort of "influence effect." Of course, this case is generally concerned with substances which have far smaller cohesive forces (*i e.*, greater volatility) than those substances whose space lattices consist of individual atoms.

e. THE METALLIC STATE

366. General.—Matter in the metallic state is distinguished by a number of physical properties which in many respects are important from both practical and theoretical standpoints. Prominent among these properties are:

High electrical conductivity, good heat conductivity, high reflective power (metallic luster), very slight permeability to light.

The metallic state is most marked in a number of elements on the left side of the periodic system; other elements whose chemical relations belong to the metalloids, *e.g.*, As, Sb, Te, show a less highly developed metallic character. A number of metallic compounds, especially the sulfides and oxides, also possess metallic properties.

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[1] See BORN, M. and GERLACH, W., *Z Physik.*, **5**, 433 (1921).

[2] *Physik. Zeit.*, **21**, 178 (1920); **22**, 302 (1921).

We are familiar with solid and liquid metals; by evaporation, however, the characteristic metallic properties disappear—for example, mercury vapor is completely transparent.

If the consideration is restricted to the solid metallic state, then a large piece of metal represents an aggregate of fine crystals, and its properties depend upon the properties of the individual crystals together with the combination of the crystals with each other.

The following will attempt to give a brief survey of those properties of metals which are characteristic for the individual, chemically homogeneous, metallic crystals, and which, therefore, appear suitable as the basis for conclusions concerning the constitution of metallic crystals and the character of the metallic state.[1] Of course, for larger metallic crystals, data which are free from objections, exist only in very limited ranges, yet for a number of properties the results obtained on crystalline, chemically uniform material, can be carried over to the metallic crystals themselves with some certainty, although some correction factors must be introduced.

The properties which depend most on the crystalline structure of the metal, especially in the combination of different metals to form alloys, are generally of a complex nature. Since their investigation is the problem of a special branch of science, metallography, they will not be considered more closely in the following.

367. Electrical Conductivity.[2]—A survey over the specific resistance w (*i.e.*, the resistance of a cube with edges 1 *cm.* long) or the reciprocal of this, the specific conductivity κ, of some substances at room temperature is given in the following summary:

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[1] A general summary, including the most important theories, is given by BAEDECKER, K., "Die elektrischen Erscheinungen in metallischen Leitern," Braunschweig (1911) (Sammlung Wissenschaft, No. 35); * C. A. KRAUS in "The Properties of Electrically Conducting Systems" (Chemical Catalog Co.) (1922)) devotes Chap. XV to a discussion of metallic substances. It contains a considerable amount of data, especially conductivity data, on pure metals, alloys and metallic compounds, together with a number of references. See also RICHARDSON, O. W., "The Electron Theory of Matter," chaps XVII and XVIII, Cambridge University Press (1914).

[2] W. Meissner has written about the more recent investigations on the thermal and electrical conductivities of metals in *Jahr Radioakt. Elektronik*, **17**, 229 (1921). * See also BROWN, W. B., *Phys. Rev.*, **22**, 171 (1923) and SIMON, F., *Z. physik. Chem.*, **109**, 136 (1924).

	w (ohms)	κ (reciprocal ohms)
Silver....... .	$1.6 \cdot 10^{-6}$	$0.62 \cdot 10^{6}$
Bismuth ..	$1.2 \cdot 10^{-4}$	$0.83 \cdot 10^{4}$
Resistance alloys.	$2\text{-}5 \cdot 10^{-5}$	$2.5 \cdot 10^{4}$
Metallic compounds (sulfides, oxides, and similar substances)..	$1.2 \cdot 10^{-4}$ and higher	$0.83 \cdot 10^{4}$ and lower
Graphite .	$2.8 \cdot 10^{-3}$	$3.6 \cdot 10^{2}$
Best conducting sulfuric acid solution (30 per cent).	1.35	0.74

It indicates that the electrical conductivity of typical metals at room temperature is about 10^5 or 10^6 times greater than that of a very highly conducting electrolyte (30 per cent sulfuric acid solution).

The strong increase in the resistance of pure metals with increasing temperature is very remarkable. At high temperatures the resistance is approximately proportional to the absolute temperature. The temperature coefficient $\frac{1}{w_{273}}\frac{dw}{dT}$ of resistance has about the same value (as a rule, a little higher) as the expansion coefficient of an ideal gas.

At ordinary temperatures the resistance curve is nearly parallel to the thermal energy content of the metal. Since the energy content is proportional only to the absolute temperature as long as the law of Dulong and Petit is fulfilled, at low temperatures a deviation from the proportionality with the absolute temperature also becomes perceptible. Grueneisen has shown that the expression

$$\frac{w}{w_{273}} = ATC_p = AT(1 + a_1T + a_2T^2)C_v =$$
$$AT\,(1 + a_1T + a_2\,T^2)\,D\left(\frac{T}{\Theta}\right) \qquad (308)$$

represents the temperature coefficient of the resistance even better than the proportionality to the energy content. A is a proportionality factor, D the Debye function, a_1 and a_2 are correction factors which are determined empirically (but which are of minor importance) and which should compensate for the difference between C_p and C_v. As the following table shows, the formula reproduces the results remarkably well. In spite of the fact that a change of several hundred fold in the temperature and 10,000 fold in the resistance is involved, the difference between the observed and the values calculated according to Eq. (308) is only a few per cent.

TABLE 83.—THE RESISTANCE RATIOS $\frac{w}{w_{273}}$ OF PURE GOLD AT DIFFERENT TEMPERATURES

$\Theta = 190 \quad a_1 = 7 \cdot 10^{-5} \quad a_2 = 13 \quad 10^{-8}$

T	$\frac{w}{w_{273}}$ obs.	$\frac{w}{w_{273}}$ calc.
11 1	0 00063	0 00063
14 3	0 00170	0 00172
18 0	0 00380	0 00427
21 5	0 00836	0 00832
57 8	0 132	0 131
75 2	0 207	0 204
91 5	0 276	0 273
169 3	0 592	0 589
273 1	1 000	1 000
573 1	2 24	2 25
1073 1	4 77	4 79
1279 1	6 03	6 03

As a rule, the same values of Θ can be used for the calculation of the resistance ratio by means of Eq. (308) as were used in calculating the atomic heat; in some cases where it is doubtful how closely the metal fulfils the condition of being monoatomic (Hg, Cd) different values of Θ are necessary.

At very low temperatures Eq. (308) fails and at a definite temperature the resistance ratio suddenly decreases very much more rapidly than corresponds to the Debye function. Just below this limiting temperature, the specific resistance reaches such a low value that it cannot be measured even with the most sensitive methods. The metal has become **"superconducting"** (Kammerlingh Onnes (1911)).[1] This superconductivity has been established for the following metals, the figures in parentheses giving the temperature at which this property occurs when only a small current load is applied in the measurement: Hg (4.1), Sn (3.78), Pb (about 6), Tl (2.3). The extremely small value of the resistance is indicated by an experiment by K. Onnes, in which the current developed in an superconducting metal loop by induction or similar means flowed for hours without appreciably decreasing. The limiting temperature at which superconductance occurs can, moreover, be influenced by various physical means (heavy current loads, external magnetic field, etc.).

368. Heat Conductivity.—The heat conductivity (Λ') of the metal which conducts best (Ag) amounts to about 1 *cal. cm.*$^{-1}$ *deg.*$^{-1}$ *sec*$^{-1}$ = 4.19 *watts cm.*$^{-1}$ *deg.*$^{-1}$ at ordinary temperatures. For good-conducting, pure metals the heat conductivity in the region of the higher temperatures depends but slightly on the temperature, at low temperatures it increases more or less rapidly. A general law for the variation with temperature has not yet been obtained, since the majority of metals have been investigated in the crystalline state and the heat conductivity appears to be very much impaired at low temperatures by the crystalline structure. The heat conductivity of a large copper crystal, which was investigated by R Schott,[2] increased about thirty-one times by lowering the temperature from 273 to 20.4° *abs.*

369. The Wiedemann-Franz Law.—For high temperatures where the electrical conductivity varies inversely proportional to the absolute temperature and the heat conductivity depends but very slightly on the temperature, there is a law stated by Wiedemann and Franz (1853) and completed by L. Lorenz (1882): the ratio $\frac{\Lambda'}{\kappa T}$ is constant and has the same value for a large number of metals. Recent measurements on pure metals at 273° give the following values for the ratio $\frac{\Lambda'}{\kappa T} \cdot 10^8$ in *watt . degree*$^{-2}$. *ohm:* Na, 2.23; K, 2.26; Li, 2.23; Cu, 2.23 to 2.42; Au, 2.35; Pt, 2.51; Pb, 2.47; Cd, 2.45. Towards lower temperatures, marked deviations from this law occur and the ratio $\frac{\Lambda'}{\kappa T}$ decreases; of course, the variation is much less than for the individual values Λ' and κ. For the copper crystal measured by Schott, the electrical conductivity increases about 1000 times between 273 and 20.4°, the heat conductivity about thirty-one times, while $\frac{\Lambda'}{\kappa T}$ decreases only to about one-half. On account of the uncertainties attached to the above conductivity measurements, it is not yet clear in what way the Wiedemann-Franz law is to be modified for low temperatures.

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[1] A summary is given by CROMMELIN, C A, in *Physik. Zeit.*, **21**, 270, 300, 321 (1920).

[2] *Verh. Deut. physik. Gesell.*, **18**, 27 (1916).

370. Thermoelectric Phenomena.—1. If the two junctions of a conducting circuit consisting of two different metals are put at different temperatures, a **thermoelectric force** is generated (Seebeck, 1821) which—provided it is not compensated by another *e.m.f.* in the circuit—according to Ohm's law results in a flow of current. The thermoelectromotive force of two metals between 273 and $T°$ may often be represented for the higher temperatures by the formula found by Avenarius (1863):

$$E = \alpha(T - 273) + \frac{\beta}{2}(T - 273)^2$$

$$\frac{dE}{dT} = \alpha + \beta(T - 273).$$

That is to say, the thermoelectromotive force per degree difference of temperature increases with increasing temperature. For pure, typical metals α attains values up to 20 *microvolts;* considerably greater values are found for alloys, metallic compounds, and elements like As, Sb, Te, and Bi. Approaching the low temperatures, $\frac{dE}{dT}$ usually decreases and appears to become practically zero even at finite temperatures, similar to the temperature coefficients of the other properties of solid bodies.

2. A counterpart to the Seebeck effect is the effect discovered by Peltier (1834). If a current is caused to flow across the junction

of two different metals, a heating or cooling occurs, depending on the direction of the current. The amount of heat developed is of the order of magnitude of about $\frac{1}{1000}$ *cal.* per coulomb. As far as can be determined from the data available at present, the effect increases with increasing temperature approximately proportional to the absolute temperature.

3. If a galvanic current flows in a homogeneous electric circuit in which a temperature drop exists, then in every volume element and depending on the direction of the current, a certain amount of heat will be given up or absorbed exclusive of heat due to resistance or Joule's heat (Thomson, 1854). The effect is still smaller than the Peltier effect and its quantitative measurement can be performed only with the aid of very sensitive methods. As a rule, the Thomson heat effect (per coulomb and a temperature drop of 1°) is of the order of magnitude of about $\pm 10^{-6}$ *cal.*

371. Optical Properties.—In a good conductor of electricity it is relatively difficult to produce an electromagnetic oscillation, since the electric field is always largely annulled by the electrical compensation due to the conductivity. If, therefore, an electromagnetic wave proceeding from a vacuum is allowed to fall upon a metallic conductor, the propagation of the wave will be highly disturbed, although in the surface layer of the metal only very small amplitudes of vibration of the electrical waves can be developed. According to the general laws for the propagation of wave motion, a "node" in the electric force must be formed in the metal surface. This is only possible through the formation of a reflected wave whose amplitude at the metal surface is approximately equal to and in the opposite direction to that of the incident wave. The greater the electrical conductivity of the metal the smaller becomes the field which can be developed at the surface, and therefore the more completely is the light reflected. The compensation of the field within the conductor often becomes more complete as the frequency becomes smaller, or, in other words, with longer period of vibration or wave lengths of the individual light.

It is, therefore, to be expected that the reflecting power of a metal is greater when its conductivity is high and the wave length of the incident light is large. The quantitative calculation based on the electromagnetic theory of light[1] leads to the formula

$$100 - R' = \frac{36.5}{\sqrt{\lambda\kappa}}, \qquad (309)$$

in which R' represents the power of reflection in per cent and the numerical values of the constants involved are so chosen that κ is expressed in reciprocal ohms and the wave length λ in centimeters.

In the range of visible light, this equation is not confirmed, yet Rubens and Hagen succeeded in showing that for light of longer wave lengths, from about $\lambda = 4 \cdot 10^{-4}$ *cm.* $= 4\mu$ upwards, it agreed completely with the observations.

When we succeed in determining the electrical conductivity of a metal theoretically from the atomic structure, then immediately one of the most important optical properties, the reflective power, becomes calculable at least for light of long wave length.

372. The Hypothesis of Free Electrons.—The electrical phenomena in metals may be explained in a far-reaching manner by the previously mentioned (see **285**) assumption that within the metals, in the openings between the atoms, are numerous freely moving electrons. This hypothesis was first mentioned by Riecke (1898) and has since been taken up by Drude, Lorentz, and numerous other investigators, especially Debye and Bohr, and has been built up into a complete theory.[2] Although the fundamental assumption of the presence of free electrons appears probable from various phenomena, especially the thermal emission of electrons, and the theory has been very useful in the explanation of other specific facts such as the Wiedemann-Franz law, in other points it leads to contradictions which at present cannot be completely accounted for. It is sufficient, therefore, to indicate the theory in its clearest and simplest form as it was developed by Drude.

It will be assumed that the electrons within the metal follow the laws which hold for gas molecules, and especially the law of energy partition; their mean kinetic energies thus amount to $\frac{mV^2}{2} = \frac{2}{3} kT$, further, the electrons undergo collisions with each other and with the metal ions, just like gas molecules; the distance which an electron can pass over freely can thus again, similar to gas molecules, be called the free path l

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[1] See BAEDECKER, *loc cit*, p 127 *et seq.*; also DRUDE, "Theory of Optics," translated by MANN and MILLIKAN, Longmans, Green & Co (1902).

[2] A summary of the new electron theory is given by SUTER, P., "Die Elektronentheorie der Metalle," Bern (1920).

If an electric force $\mathfrak{K} = Xe$ acts on such an electron while the time between two collisions is $\tau = \frac{l}{V}$, then the electron undergoes a total increase of velocity which is

$$\Delta V = \frac{\mathfrak{K}}{m}\tau = \frac{Xe}{m}\frac{l}{V}. \tag{310}$$

The velocity components of the electrons in the direction of the electric field are, therefore, on the average, $\frac{\Delta V}{2} = \frac{1}{2}\frac{Xe}{m}\frac{l}{V}$ greater than the other velocity components

If N' electrons are present in 1 $cm.^3$, an amount $N'e\frac{\Delta V}{2}q$ of electricity will move through the cross-section q of the conductor in unit time as a result of the $\frac{\Delta V}{2}$ times greater velocity of the electrons in the direction of the electric field; *i e*, a current will flow whose strength is given by

$$i = N'e\frac{1}{2}\frac{e}{m}\frac{l}{V}Xq = \frac{N'e^2}{2m}\frac{l}{V}\frac{\Delta E}{\Delta x}q.$$

Now putting $q = 1$ and $\Delta x = 1$, then according to Ohm's law the term $\frac{2mV}{N'e^2l}$ is the specific resistance; for the specific conductivity, therefore (by introducing the law of equipartition of energy $\frac{1}{2}mV^2 = \frac{3}{2}kT$):

$$\kappa = \frac{1}{2}\frac{N'e^2l}{mV} = \frac{1}{6}\frac{N'e^2Vl}{kT}. \tag{311}$$

The heat conductivity of a metal may be calculated by means of the electrons in the same way as that of gas by means of the gas molecules In an ordinary gas or "electron gas" there exists a temperature gradient $\frac{dT}{dx}$ or an energy gradient $\frac{dU}{dx} = \frac{3}{2}k\frac{dT}{dx}$. With a mean free path l, those electrons will pass through the cross-section of the conductor at the point 0 whose energy is not U_0, but $U_0 \pm \frac{dU}{dx}l$. The number of electrons which in unit time pass through unit cross-section is $\frac{1}{3}N'V$, since it may be assumed schematically, as in **48**, that of all the electrons only one-third possess a velocity at right angles to the observed cross-section In unit time there will thus pass through the unit cross-section an amount of energy which is

$$\Delta U = \frac{1}{3}N'Vl\frac{dU}{dx} = \frac{1}{2}N'Vlk\frac{dT}{dx}.$$

Since by definition the heat conductivity represents the amount of energy passing a unit cross-section at a unit difference of temperature, it follows directly that

$$\Lambda' = \frac{1}{2}N'lVk.$$

Now taking the ratio $\frac{\Lambda'}{\kappa T}$, then

$$\frac{\Lambda'}{\kappa T} = 3\left(\frac{k}{e}\right)^2 = 3\left(\frac{R}{\mathfrak{F}}\right)^2. \tag{312}$$

If $R = 8.31 \cdot 10^7$, $\mathfrak{F} = 9650$ *e.m u.* and we then get $\frac{\Lambda'}{\kappa T} = 2.24 \cdot 10^8$ *abs. units* $= 2.24 \cdot 10^{-8}$ (*watt deg*$^{-2}$ *ohm*).

The agreement between this value and the one found in **369** as the result of observations is remarkable.

373. The Theory of Thermoelectric Phenomena.—The hypothesis of free electrons is also useful in the explanation of the thermoelectric phenomena. If the presence of free electrons is assumed in metals, then in different metals they would have different concentrations and therefore unequal tendencies for expansion. At the junction of two metals the electrons would pass from the one metal to the other, *i.e.*, the one metal is differently charged electrically against the other and a **contact potential** develops between them. This potential is generally of the order of 10^{-3} *volts*. Strange to say, an exact measurement, as a rule, involves such difficulties that a summary of the considerable amount of data is of no value for the present purpose.

If a closed circuit is formed of two metals and if the two junctions are kept at the same temperature, then, at the junctions, potential differences develop which are equal in magnitude but opposite in direction, so that no current flows in the circuit. In case the concentration and the velocity of the electrons in the two metals do not vary in exactly the same way with the temperature, then a constant potential will be established at the hotter junction which is different from that of the colder; thus the *e.m f.* of the two no longer balance each other and a thermoelectric force remains which is able to maintain a current in the circuit.

The Peltier effect may also be explained from the conception that, by the transfer of a certain amount of electrons through the junctions of two metals, the electrons will be expanded or compressed. The work of compression or expansion can make itself effective only as a positive or negative heat effect. The Peltier effect is thus directly comparable to the Joule-Thomson effect in gases (see **88**).

The Thomson heat effect is composed of two parts:

1. From the heat equivalent of the work which corresponds to the expansion or compression of the electrons in passing from the warmer to the colder parts of the metal.
2. From the kinetic energy which the electrons carry with them in their migration due to the electric current.

If only the latter amount were involved in the matter, the Thomson effect would have the same sign in all metals, but in some metals it is positive, in others negative.

374. The Hypothesis of an Electronic Lattice.—But in opposition to the varied kinds of results which the hypothesis of free electrons could reproduce, there are several considerations based upon the following:

If the energy partition law holds true for electrons, the presence of the electron gas must indicate itself by greater atomic heats for the metals than for non-metals. But for something of this sort, especially at low temperatures, no indication exists; the Debye T^3-law[1] holds with great accuracy for both metals and non-metals *at low temperatures*, at least as far as monoatomic substances are concerned.[2]

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[1] If this discovery is to be brought into agreement with the hypothesis of free electrons, then it must be assumed unconditionally that only very few electrons are present. But in order to explain the excellent electrical conductivity with them, it is necessary that their free paths be quite considerable (see Eq (311)). Formerly, this seemed to be unpermissible but, according to the more recent results on the behavior of electrons as compared with atoms, this conception must be given greater consideration. At present one may dare to imagine that the electrons do not move in straight lines in the interstices between the atoms, but circle about the individual atoms; yet the orbits about the various atoms are so interlocked that forthwith an electron can pass a large number of atoms (around each individual atom the electron would describe an approximately semicircular path) The mean free path (in the sense of **370**) can no longer be understood to be merely the path from one atom to another, but the average distance through which the electron passes before it gives up its energy (which was received from an electric field). From such a viewpoint it seems conceivable that this first takes place after passing by numerous atoms, so that a large free path will be reasonable.

[2] * After an exhaustive study of the specific heat data, Eastman, Williams, and Young (*J. Am. Chem. Soc*, **46**, 1184 (1924)) find that *at high temperatures* the specific heat values are greater than the classical value $C_v = 3R$ by amounts considerably larger than the experimental errors of the

It has, therefore, been attempted to replace the hypothesis of free electrons either completely with another or at least to give up the validity of the law of equipartition of energy. In all cases, the remarkable results of Eq. (312) must be given up, since the constant k of the equipartition law plays a decisive part in it, and the numerous agreements between observations and calculation must be considered as something accidental.

One possibility of explaining the high heat conductivity of a metal without the use of the energy partition law consists in the assumption of an **electron lattice** which is superimposed on the lattice of the atom ions.[1] The electrons on the points of the lattice perform relatively rapid vibrations (null point vibrations, see **71**), which at low and ordinary temperatures do not contribute to the atomic heat. The excellent heat conductivity of metals exists due to the whole electron lattice, which is coherent in itself, acting as a unit in propagating the heat waves just like elastic waves. Other arguments can also be advanced in favor of the assumption of an electron lattice. For example, the fact that the atoms or ions of most metals in crystalline form can be arranged in a face-centered cubic lattice (see **358**) indicates that, theoretically, metals have the same lattice structure as the halogen-alkali salts but that in the metals the halogen ion is replaced by an electron (Figs. 94 and 95). But, on the other hand, the high electrical conductivity of metals is not easily understood by means of the lattice hypothesis; since the electron lattice must be fixed in a stable position between the lattices of the metal ions, it would be expected that a certain amount of energy would need to be expended in order to overcome the force which holds it in its stable position. There should, therefore, be a lower limit of electrical potential below which no cur-

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determinations. These authors compare several explanations which have been proposed to account for this, but believe that the most probable one is that the loosely bound electrons have the power to absorb appreciable quantities of energy as first suggested by Konigsberger (*Z Elektrochem.*, **17**, 289 (1911)) The application of this idea is limited to temperatures not too near the melting points, yet high enough that C_v should normally be nearly equal to $3R$.

[1] LINDEMANN, F. A , *Phil. Mag.*, **29**, 126 (1915); BORELIUS, G., *Ann. Physik* , **57**, 231, 278 (1918); **58**, 489 (1919); HABER, F., *Berl. Akad. Ber.*, 506 (1919).

rent could flow. As a matter of fact, nothing of this nature has been observed in metals, and Ohm's law holds even for the lowest potentials.

375. Summary.—On the whole, *the electrical and many other properties of metals lend a very high degree of probability to the assumption of the presence of electrons which, within the metal, are free from the atoms and which possess a considerable independence.* The numerous efforts spent in obtaining a more exact knowledge of the arrangement and motions of these electrons have produced no result which is completely satisfactory up to the present moment; each of the more detailed theories have led previously either to some contradictions or they were burdened with special assumptions which on more general grounds did not appear reasonable from the very beginning.

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